

THE EFFECT OF VISCOELASTIC SURFACTANTS USED IN CARBONATE
MATRIX ACIDIZING ON WETTABILITY

A Thesis

by

OLADAPO OLISE ADEJARE

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2012

Major Subject: Petroleum Engineering

The Effect of Viscoelastic Surfactants Used in Carbonate Matrix Acidizing on
Wettability

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ABSTRACT

The Effect of Viscoelastic Surfactants Used in Carbonate Matrix Acidizing on Wettability.

(May 2012)

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Carbonate reservoirs are heterogeneous; therefore, proper acid placement/diversion is required to make matrix acid treatments effective. Viscoelastic surfactants (VES) are used as diverting agents in carbonate matrix acidizing. However, these surfactants can adversely affect wettability around the wellbore area.

Lab and field studies show that significant amounts of VES are retained in the reservoir, even after an EGMBE postflush. Optimizing acid treatments requires a study of the effect of VES on wettability.

In a previous study using contact angle experiments, it was reported that spent acid solutions with VES only, and with VES and EGMBE are water-wetting.

In this thesis, we studied the effect of two amphoteric amine-oxide VES', designated as "A" and "B" on the wettability of Austin cream chalk using contact angle experiments. We extended the previous study by using outcrop rocks prepared to simulate reservoir conditions, by demonstrating that VES adsorbs on the rock using two-

phase titration experiments, by studying the effect of temperature on wettability and adsorption, and by developing a detailed procedure for contact angle experiments.

We found that for initially oil-wet rocks, simulated acid treatments with VES “A” and “B” diversion stages and an EGMBE preflush and postflush made rocks water-wet at 25, 80, and 110°C. Simulated acid treatments with a VES “A” diversion stage only made rocks water-wet at 25°C. Our results suggest that both VES formulations cause a favorable wettability change for producing oil.

The two-phase titration experiments show that both VES “A” and “B” adsorb on the rock surface.

From our literature review, many surfactant wettability studies use contact angle measurements that represent advancing contact angles. However, wettability during stimulation is represented by receding contact angles. Results of static receding contact angles may be misinterpreted if low oil-acid IFT's cause oil droplets to spread. Spreading could be a reflection of the effect of the surfactants on the fluid-fluid interface rather than the rock-fluid interface. The new procedure shows the effect of VES and EGMBE on the rock-fluid interface only, and so represents the actual wettability.

DEDICATION

To my parents and siblings

ACKNOWLEDGEMENTS

I would like to thank my committee chair, Dr. Hisham Nasr-El-Din, for giving me the opportunity to work with him. I would also like to thank my committee members, Dr. A. Dan Hill and Dr. Mohmoud El-Halwagi, for their support throughout the course of this research.

I would like to thank my colleagues in Dr. Hisham's research group, in the PE Department, and the PE departments' facilities staff for their guidance in using lab equipment and for many useful discussions.

Finally, I would like to thank my parents and siblings for their support throughout my studies.

NOMENCLATURE

$\cos \theta_{ow}$	Cosine of oil-spent acid contact angle
d	Oil-droplet diameter for spinning drop tensiometer IFT calculations
P	Rotational speed of spinning drop tensiometer
S_{os}	Oil spreading coefficient
$\Delta\rho$	Density difference between oil and spent acid in spinning drop tensiometer
γ_{ow}	Oil-spent acid interfacial tension
γ_{os}	Oil-rock interfacial tension
γ_{ws}	Spent acid-rock interfacial tension

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1 INTRODUCTION

The objective of this study is to determine the effect of viscoelastic surfactants (VES) used as a diverting agent in carbonate matrix acidizing on wettability.

Acidizing fluid additives should be selected to prevent wettability changes that reduce productivity. Chemical treatments designed to enhance well performance can often instead create another form of damage (Nasr-El-Din, 2005).

1.1 Matrix acidizing

Matrix acidizing is used to improve production from oil and gas wells and to improve injection into injection wells.

Wells with impaired productivity are identified and the cause of the impairment diagnosed. If the impairment results from low reservoir pressure, low permeability or inadequate tubing size, matrix acidizing cannot enhance productivity (Nolte and Economides, 2000). Productivity impairment resulting from partial completions or pseudo-skin factors can also not be removed by matrix stimulation. Productivity can be enhanced by matrix acidizing if the impairments result from formation damage. The type of damage can be discerned from the well history file, or from materials recovered from the well. Typical sources of damage are drilling and completion fluids.

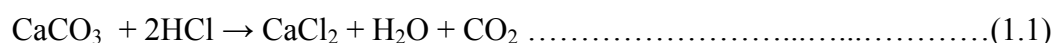
An acid or solvent is injected into the reservoir below the fracture pressure to

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dissolve materials that impair well performance in sandstones, or to create channels that bypass the damage in carbonates. Fracture treatments (above reservoir pressure) are more cost effective in low permeability reservoirs when greater reductions in skin are required to achieve the targeted production rate.

The treating fluid is then selected depending on the type of damage and the formation (carbonate or sandstone). Chemical additives are selected to enhance the performance of the treating fluid e.g. water-wetting surfactants may be added to ensure a favorable wettability, or corrosion inhibitors may be added to protect tubulars against corrosion.

Carbonate reservoirs are stimulated using primarily hydrochloric acid (HCl) to enhance productivity. At the optimum injection rate, the reaction of HCl with the calcite (**Eqn. 1.1**) or dolomite rocks enhances productivity by creating high conductivity pathways into the wellbore called wormholes.



A wormhole is a large, empty channel that can penetrate several feet into the formation, and bypass the damage.

1.2 Need for diversion

Diversion is needed because of permeability contrasts in the reservoir. Permeability contrasts may result from different depths of damage and reservoir heterogeneity. Diversion may also be needed in reservoirs with different lithology's because the reaction rate between calcite and HCl is an order of magnitude greater than

between HCl and dolomite (Taylor et al., 2004). In addition to these factors, in carbonates rocks, natural fractures can act as thief zones.

Because of permeability and lithological contrasts, zones nearer the point of injection of acid will be stimulated first, and thus take more acid than zones further away (Jones and Davies, 1998). In addition, as stimulation progresses, the permeability contrast becomes more adverse as acid flows preferentially to the already stimulated zones.

Proper acid placement is required to make acid treatments effective. Without proper placement, more acid would be required to achieve the same amount of stimulation (Economides and Nolte, 2000). In addition, improper placement will result in inefficient damage removal, with the most damaged zones getting the least amount of stimulation. Non-uniform stimulation can also lead to a high drawdown that could cause early, undesirable gas and water production (Al-Anzi et al., 2004).

Placement is achieved by mechanical means, such as a combination of coiled tubing and packers. Mechanical placement techniques can only be deployed in the wellbore and crucially do not control fluid flow in the reservoir. Furthermore, mechanical placement may not be deployable in open hole or slotted liner completions, and may be expensive (Chang et al., 2007).

Placement can also be achieved by chemical means, which has the advantage over mechanical placement that it controls fluid flow in the reservoir. Chemical placement methods include foams, emulsified acid, and gelled acid. They work by building up viscosity to block high permeability zones, thus diverting acid to low

permeability zones. Diversion is also achieved by a reduction in the reaction rate between the acid and the rock resulting from the acids' increased viscosity (Jones and Davies, 1998). Viscoelastic surfactants (VES) and polymers are a type of in-situ gelled acid.

VES is preferred to polymer gels because it does not require a cross-linker that may precipitate, and its viscosifying chemistry is much simpler (Caweizel, 2007). Also, polymers have been shown to leave residues on the core face and in the core (Taylor and Nasr-El-Din, 2002), and so may cause formation damage. In contrast, VES molecules are much smaller and so are less likely to leave a residue in the reservoir. Emulsified acids do not dissolve as much iron as regular acid, so that the concentration of potentially damaging iron ions that enter the formation is less (Nasr-El-Din et al., 2000). They also do not leave residue in the reservoir. However, VES-based acids achieve much higher viscosities than emulsified acids.

VES-based acid systems divert HCl during carbonate matrix acidizing because their viscosity increases as the pH increases (Al-Anzi et al., 2004; Caweizel, 2007) forming a thick gel as the acid spends in the presence of divalent cations. The buildup of viscosity in the highly reactive zone due to its high permeability or faster reacting lithology will result in diversion of acid into low permeability or slower reacting lithological zones. This increases the uniformity of the sweep, and improves the acid treatment.

1.3 VES retention

Lab and field studies suggest that VES is retained in the reservoir.

The use of VES-based acid fluids in carbonate matrix acidizing has caused damage in low permeability oil formations. Nasr-El-Din et al. (2006a) reported that a 7 vol% VES loading was suspected to have caused a permanent plug in the formation.

Mutual solvents significantly lower the viscosity of VES (Li et al., 2010a) and so potentially aid in its clean up when the well is flowed back. In a lab study, cores treated with HCl with a VES concentration of 3-4 vol% required no mutual solvent to regain their initial permeability to water. Cores treated with acid with a 6-vol% VES concentration required a mutual solvent postflush to regain their initial permeability.

Material balance calculations from coreflood experiments using VES-based acids showed that only 22% of VES was removed from a 20 in. carbonate core after it was treated with a mutual solvent solution (Yu et al., 2010).

Crews and Huang (2007) showed that seawater did not break a VES gel in a lab test. Huang and Crews (2008) showed that a crude oil did not break down the viscosity of the VES gel. In both experiments, internal breakers were needed to break the VES gel.

Experiments by Huang and Crews (2008) suggested that unbroken VES gels probably have a very high viscosity at low shear rates, and a lot of mixing that is unlikely to occur in porous media is required for reservoir fluids to break the gel. Retained VES can cause wettability changes in the near well region.

1.4 Wettability

For a solid-fluid-fluid system wettability is the relative preference of a surface to be covered by one of the fluids under consideration (Morrow, 1991). Rocks are considered oil-wet if the surface shows a stronger preference for oil than for water. The rock is considered water-wet if it shows a greater preference for water than for oil.

Wettability is extensively studied in petroleum engineering because it affects the distribution and flow of fluids through the rock (Owens and Archer, 1971; Morrow et al., 1986; Anderson, 1987; Esfahani and Haghighi, 2004; Zhang Leslie et al., 2006).

Wettability is measured by qualitative and quantitative techniques (Anderson, 1986). Quantitative methods include contact angles, Amott, and USBM method. An example of a qualitative measurement is the relative permeability method.

Contact angles, Amott tests, USBM experiments, and relative permeability measurements have been used to study reservoir wettability (Treiber and Owens, 1972; Lichaa et al., 1992).

Contact angle experiments are the most effective method for studying the effect of pure fluids on artificial core wettability. They are also the best choice for studying the effect of temperature, pressure and brine chemistry on wettability.

Amott and USBM methods give the average wettability of core samples. Wettability measurements based on relative permeability curves are most effective for strongly wetted systems.

1.5 Importance of wettability in well stimulation

Wettability changes due to stimulation fluids are recognized as a form of induced formation damage. Wettability affects the clean-up of stimulation fluids by reservoir fluids, and the subsequent production of reservoir fluids. The wettability and relative permeability of a formation at any saturation depend on the coatings of surface-active agents in the reservoir or from injected fluids (Economides and Nolte, 2000).

In general, neutral wettability is the ideal wettability state to enhance the displacement of stimulation fluids from the near-well region, while water-wetness is the preferred wettability state for the optimum production of oil.

1.6 VES formulations

We studied the effect of two amphoteric amine-oxide viscoelastic surfactants on wettability.

The first is designated as VES “A”. A US patent is described by Caweizel (2007), and rheological properties were described by Li et al. (2010a) and Li et al. (2010b) respectively. Field applications are described in Nasr-El-Din et al. (2006a), Nasr-El-Din et al. (2006b), and Nasr-El-Din et al. (2006c). Spent acid solutions with VES “A” maintain viscosity at temperatures up to 80°C.

The second is designated as VES “B”, and was designed for temperatures up to 150°C. There are no publications on it yet.

Two major characteristics of surfactants are their ability to form micelles (Nasr-El-Din et al., 2008) and their surface activity (Rosen and Dahanayake, 2000). Both

characteristics result from the surfactants' structure, which consists of a hydrophilic head and a hydrophobic tail. Surfactants form micelles in aqueous solutions to shield their tail from the aqueous solution. Surface activity may occur because of electrostatic adsorption between the surfactants polar head and the rock surface, or by hydrophobic bonding between the surfactant tail and the rock. Surface activity of retained surfactant (Section 1.3) may result in wettability changes.

VES is used in diversion because in aqueous solutions they build up viscosity due to structural changes that depend on the properties of the solution. They form spherical micelles and have low viscosity in live acid hydrocarbons (Nasr-El-Din et al., 2008). They form wormlike micelles as the pH of the solution increases and the divalent cation concentration increases due to the reaction between HCl and the carbonate rock. At the end of the treatment, hydrocarbons or mutual solvents break down the structure of the VES gel to spherical micelles and reduce the viscosity. This allows the production of hydrocarbons.

1.7 Prior studies

Lungwitz et al (2007) reported that spent acid solutions with VES only were water-wetting. They also reported that spent acid solutions with VES and EGMBE with a 1:1 ratio by volume, was strongly water-wetting. The spent acid solutions represent the mixing that occurs after an acid treatment.

1.8 Objective and outline

The objective of this thesis is to study the effect of two amphoteric amine-oxide VES' (described in Section 1.5) on wettability of Austin cream chalk rocks.

We extended the prior study by using rocks prepared to simulate reservoir conditions, by demonstrating that VES adsorption occurs on rocks, providing a detailed procedure for contact angle experiments, and studying the effect of temperature on wettability and adsorption.

Experiments were performed at temperatures from 25 to 110°C and at 500 psi. The VES concentration was varied from 1-6 vol %. The EGMBE concentration was varied from 1-10 vol%.

In Section 2, the two-phase titration technique was used to measure VES adsorption on Austin Cream Chalk rocks at 25, and 80°C.

In Section 3, we showed that low oil-acid IFT's in spent acid solutions with VES and EGMBE cause oil droplets to spread in static receding contact angle experiments. From our literature review, many surfactant wettability studies use contact angle measurements that represent advancing contact angles. However, wettability during stimulation is represented by receding contact angles. Results of static receding contact angles may be misinterpreted if low oil-acid IFT's cause oil droplets to spread. Spreading could be a reflection of the effect of the surfactants on the fluid-fluid interface rather than the rock-fluid interface. The new procedure shows the effect of VES and EGMBE on the rock-fluid interface only, and so represents the actual wettability.

We applied the new procedure to study the effect of spent acid with VES “A” and EGMBE on wettability. This experiment represents the mixing of fluids after an acid treatment, and the results are compared with those of Lungwitz et al.(2007). The new procedure can be applied to dynamic contact angle experiments like the DDDC technique (Rao and Girard, 1996) for which static receding contact angle measurements precede dynamic measurements.

Acid treatments consist of multiple treating fluid-diverting sequences. Therefore, in Section 4, we simulated acid treatments with VES diversion only, and with VES and an EGMBE preflush/postflush using the new procedure. The results of these experiments represent the wettability state of the rock-fluid interface just as oil starts to displace spent acid.

2 TWO-PHASE TITRATION EXPERIMENTS

In this Section, we demonstrate that both VES “A” and “B” adsorb on the surface Austin Cream Chalk rocks using two-phase titration experiments. Adsorption experiments were conducted at 25 and 80°C for VES “A” and VES “B”. VES “A” adsorbs more than VES “B”. Adsorption is reduced by temperature, with the reduction being more significant for VES “B”.

2.1 Experimental studies

2.1.1 Two-phase titration

The two-phase titration experiment we used was developed by Yu and Nasr-El-Din (2009) to measure the concentration of a carboxybetaine surfactants.

The titrant is added to a solution consisting of the surfactant, a blue organic phase and a green aqueous phase. At the end-point, the color of the organic phase changes to purple (**Fig. 2.1**).

Before titration, the solution consists of VES, the indicator solution, and chloroform. The aqueous, indicator phase consists of disulphine blue and ethidium bromide, while the organic phase consists of chloroform. When the surfactant complexes with disulphine blue molecules in the aqueous phase, it displaces into the organic phase, and shows a blue color.

The addition of the titrant (sodium dodecanesulphonate) causes the blue color of the organic phase to fade. At the end-point, titrant molecules complex with the ethidium

bromide in the aqueous phase and displace into the organic phase, making the organic phase turn purple.

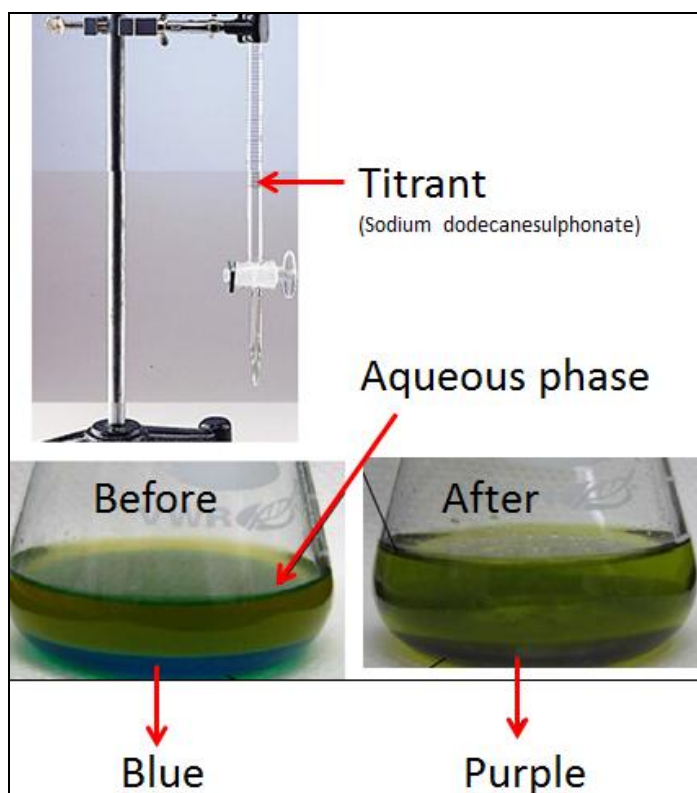


Fig.-2.1 Two-phase titration experiment

VES adsorption was determined by comparing titrant volumes of spent acid solutions before and after adsorption on the rock. There is a linear relationship between carboxybetaine VES volumes and titrant volumes passing through the origin (Yu and Nasr-El-Din, 2009). The volume of VES “A” and “B” adsorbed was calculated from calibration curves determined from a similar relationship between the VES “A” and “B” concentration and the titrant volume.

2.1.2 Porous media preparation

Austin cream chalk from the Edwards Limestone outcrop was used in our experiments. The rock samples were prepared to simulate reservoir conditions (Tiab and Donaldson, 1996) by using a centrifuge to simulate brine and oil drainage and imbibition and an oven to simulate reservoir temperature (Fig. 2.2).

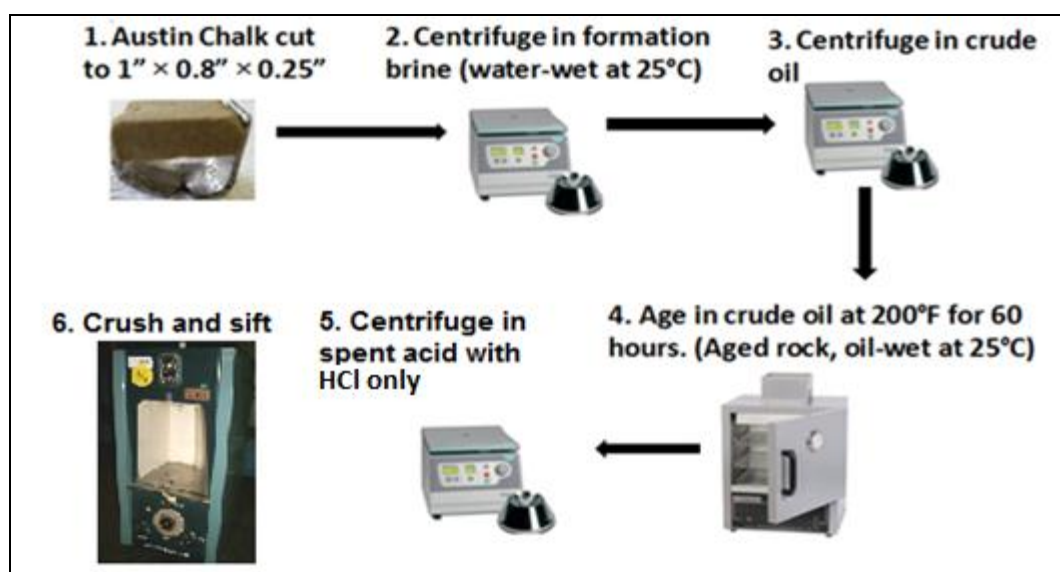


Fig.-2.2 Rock sample preparation

We cut the samples to dimensions of approximately 1 in. \times 0.8 in. \times 0.25 in. (step 1, Fig. 2.2) and air- vacuumed them in formation brine for 30 minutes at a pressure of - 25 psi (step 2, Fig. 2.2). Brine-saturated samples are water-wet at room temperature.

Table 2.1 shows the formation brine composition.

Table 2.1 Formation brine composition	
Salt (TDS 230,000 ppm)	Concentration (mg/l)
NaCl	127,523.3
CaCl ₂ ·2H ₂ O	109,162.66
MgCl ₂ ·6H ₂ O	35,657.7
BaCl ₂	15.16
Na ₂ SO ₄ *	159.69
NaHCO ₃ *	483.26
SrCl ₂ ·6H ₂ O	3,149.41
* dissolved separately to prevent precipitation	

We centrifuged the brine-saturated samples at 3,000 rpm for 30 minutes to irreducible brine saturation. We then centrifuged them in crude oil at 3,000 rpm for 30 minutes to saturate them with oil (step 3, Fig. 2.2). Finally, they were aged in oil at 200⁰F for 60 hours (step 4, Fig. 2.2). The aged rocks were oil-wet at room temperature.

The rocks were centrifuged in a spent acid solution with HCl only for 20 minutes to simulate the flow of the main treating fluid through the rock (step 5, Fig. 2.2).

The rocks were then crushed with a mortar and pestle. The crushed rocks were sieved for 15 minutes using an ATM Lab Sonic Sifter (Step 6, Fig. 2.2). Sifted rocks with mesh sizes from 140 to 325 (particle size 0.106 to 0.045 mm) were used for adsorption experiments.

2.1.3 Fluid preparation

The indicator solution and titrant used in the two-phase titration experiments were prepared as described by Yu and Nasr-El-Din (2009).

ACS grade chemicals were used to prepare formation brine. Spent acid was prepared from ACS grade dihydrous calcium chloride (CaCl₂), HCl, and calcium

carbonate (CaCO_3). All solutions were prepared using de-ionized water with a resistivity $\geq 17.8 \text{ m}\Omega\text{-cm}$ at 25°C .

We used surfactants VES “A” and “B” described in Section 1.5.

The crude oil used was sour oil from West Texas field. Its viscosity and density are 3.35 cp and 0.794 g/cm^3 respectively at 80°C .

The pH at the surface of the rock when acid reacts with carbonate is about 4.5 (Nasr-El-Din et al., 2009), therefore spent acid solutions used for contact angle and IFT measurements had a pH between 4 and 5.

Spent acid solutions were prepared from the reaction products of 20 wt.% HCl and CaCO_3 as described by Nasr-El-Din et al.(2008) and Chang et al. (2001). We used the following procedure:

1. Add calcium chloride to de-ionized water and stir with a magnetic stirrer.
2. Add HCl until pH is between 4 and 5.

Continuing from step 2 above, spent acid solutions with HCl and VES only was prepared as follows:

3. Add desired volume percent of VES.
4. Stir for 30-45 minutes with a magnetic stirrer until a thick gel is formed.
5. Transfer to a blender, and blend for a few seconds. This step removes most of the air bubbles.
6. Centrifuge at 3,000 to 6,000 rpm to remove the remaining air bubbles.

2.1.4 Procedure for two-phase titration experiments

Static adsorption tests were performed to determine surfactant adsorption. The procedure was adapted from Scamehorn et al. (1982), Somasundaran and Hanna (1985) and Al-Hashim et al. (1988).

1. Place 3g of crushed rock (from step 6, Fig. 2.2) in a centrifuge tube.

At 25°C,

2. Add 10 cm³ of spent acid with VES into the centrifuge tube.
3. Hand-shake for 20 minutes.
4. Centrifuge for 5 minutes at 5000 rpm.
5. Decant supernatant.
6. Centrifuge supernatant for 15 minutes at 5000 rpm to remove fine particles.

At 80°C from step 1,

7. Place the centrifuge tube in the oven for an hour at 80°C to heat the rock particles up.
8. Repeat step 2 to 6 above.

From steps 6 at 25°C, and step 8 at 80°C,

9. Siphon off 0.2 cm³ of supernatant with a pipette, and transfer it to a beaker.
10. Add 4.8 cm³ of deionized water
11. Add 5 cm³ of acid blue indicator
12. Add 0.1 cm³ of Tetraoxosulphate VI acid (H₂SO₄)
13. Add 7.5 cm³ of chloroform
14. Add 5 cm³ of ethanol

15. Add titrant until the aqueous phase turns purple. Record the titrant volume.

2.2 Surfactant adsorption

Surfactant adsorption is affected by temperature, wettability, rock type, brine concentration, cation concentration among other factors (Mannhardt and Novosad Jerry, 1994). Therefore, adsorption experiments with surfactants and rocks should be performed under conditions that closely simulate reservoir conditions.

2.2.1 Effect of temperature

Adsorption is an exothermic process (Bartell et al., 1951), so an increase in temperature decreases adsorption. On the other hand, increasing temperature reduces the solubility of the surfactant, so more surfactant may adsorb on the surface of the rock as temperature increases.

2.2.2 Effect of wettability

Surfactant adsorption is generally greater on hydrophobic surfaces than on water-wet surfaces. This is because of the easier displacement of interfacial water from the hydrophobic surface by the surfactant.

2.2.3 Adsorption mechanisms for amphoteric surfactants on carbonates

Previous studies concluded that a complete explanation for the results of the adsorption of amphoteric surfactants on carbonates was not possible; however, electrostatic adsorption is usually inferred from experimental results.

A study of the adsorption of amphoteric betaine and sulphobetaine surfactants on dolomite and limestone suggested that electrostatic interactions of both cationic and

anionic groups with the solids and complexation of the surfactant with divalent ions in solution or at the carbonate surfaces are likely to contribute to adsorption (Mannhardt et al., 1992).

Possible adsorption mechanisms of amphoteric surfactants on carbonates were illustrated by Mannhardt et al. (1993). On Indiana limestone, which is negatively charged in a NaCl solution, adsorption is by electrostatic attraction between the cationic head of the surfactant and the rock. Calcium ions in the solution or from the rock allow complexation between the surfactants' anionic group. On the positively charged limestone, adsorption is with the anionic group of the surfactant.

2.3 Results

We present calibration curves for VES "A" and "B" and adsorption results for VES "A" and "B" at 25 and 80°C.

2.3.1 Calibration curve for VES "A" and VES "B"

The titrant volume required to reach the end-point for 0.2 cm³ of spent acid with 0.5 vol% VES "A" is shown in **Table 2.2**. The average of two readings (7 cm³) was used. The titrant volume for 0.2 cm³ of 0.4 vol% VES "A" was also recorded.

Table 2.2 Titration volumes for 0.2 cm ³ of a spent acid solution with VES "A"				
	Titration 1 (0.5 vol %)	Titration 2 (0.5 vol %)	Average	Titration 3 (0.4 vol %)
Titrant volume (cm ³)	7	7	7	5.7

The titrant volumes in Table 2.2 are plotted against VES concentration in **Fig. 2.3**. Assuming a linear relationship passing through the origin, the calibration curve shows that 14.098 cm^3 of titrant is needed to reach the end-point for 0.2 cm^3 of 1 vol% VES “A”.

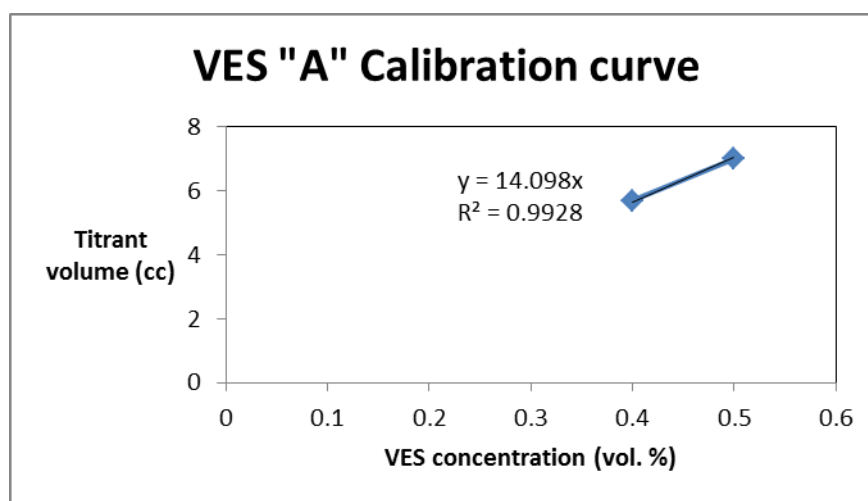


Fig.-2.3 Calibration curve for VES “A” (Values from Table 2.2)

Similarly, for VES “B”, the titrant volume required to reach the end-point is shown in **Table 2.3**. The average of two readings (6.7 cm^3) was used. The titrant volume for 0.2 cm^3 of 0.4 vol% VES “A” was also recorded.

Table 2.3 Titration volumes for 0.2 cm^3 of a spent acid solution with VES “B”				
	Titration 1 (0.5 vol %)	Titration 2 (0.5 vol %)	Average (0.5 vol %)	Titration 3 (0.4 vol %)
Titration volume (cm^3)	6.7	6.7	6.7	5.5

The titrant volumes in Table 2.3 are plotted against VES concentration in **Fig. 2.4**. Assuming a linear relationship passing through the origin, the calibration curve shows that 13.537 cm³ of titrant is needed for 0.2 cm³ of 1 vol% VES “B”.

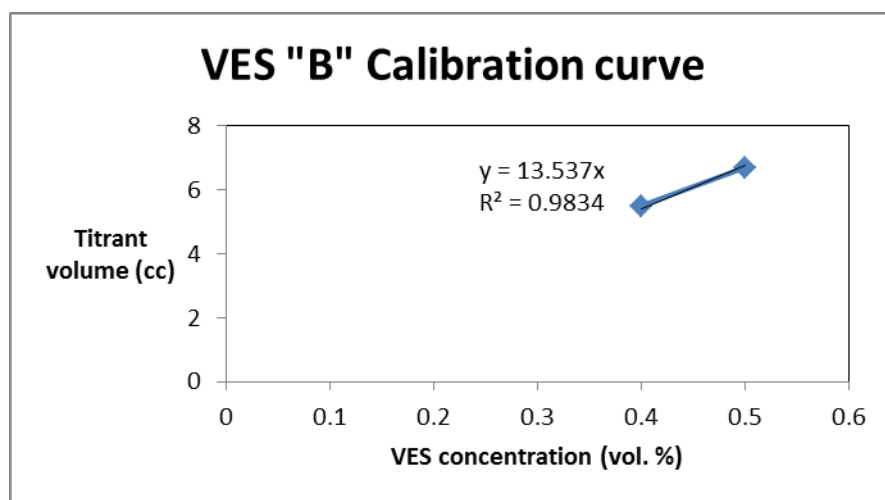


Fig.-2.4 Calibration curve for VES “B” (Values from Table 2.3)

2.3.2 Adsorption of VES “A” at 25°C

The results of titration of 0.2 cm³ of supernatant after 20 minutes of shaking with 3 grams of Austin cream chalk at 25°C is shown in **Table 2.4**.

The average of two titrations was used. The vol% of VES after adsorption in Table 2.4 was obtained by interpolation from the calibration curve in Section 2.3.1. It was reduced by surfactant adsorption from 0.5 vol % to 0.36 vol %.

Table 2.4 Titration volumes for 0.2 cm ³ of a spent acid solution with 0.5 vol% VES “A” after adsorption at 25°C				
	Titration 1	Titration 2	Average	vol % of VES after adsorption (Interpolated from Fig. 2.3)
Volume (cm ³)	5	5.1	5.05	0.36

The mass of VES adsorbed per unit mass of rock is calculated in **Table 2.5**. 4.7 mg of VES “A” adsorbed per unit gram of the rock.

Table 2.5 Calculation of mass of VES per unit mass of rock and per unit area of rock			
Vol. % Before adsorption	0.5	vol%	A
Vol. % After adsorption	0.358206838	vol%	b (Table 2.4)
Vol of VES adsorbed	0.014179316	Cc	$c=(a-b)/10$
Density of VES	0.99	g/ cm ³	d (given)
mass of VES	0.014037523	G	$e=c*d$
mass of VES	14.03752305	Mg	$f=e*1000$
mass of rock	3	G	h (given)
mass of VES per unit mass of rock	4.68	mg/g	f/h

2.3.3 Adsorption of VES “A” at 80°C, VES “B” at 25°C, and VES “B” at 80°C

Experiments and calculations in Section 2.3.2 were repeated for VES “A” at 80°C, and for VES “B” at 25 and 80°C.

The mass of VES “A” adsorbed per unit mass of rock at 80°C was 3.04 mg/g; the mass of VES “B” adsorbed per unit mass of rock at 25°C was 2.85 mg/g and the mass of VES “B” adsorbed per unit mass of rock at 80°C was 0.90 mg/g.

2.3.4 Analysis

The mass of VES adsorbed per unit mass of rock from Sections 2.3.2-3 are plotted in **Fig. 2.5**.

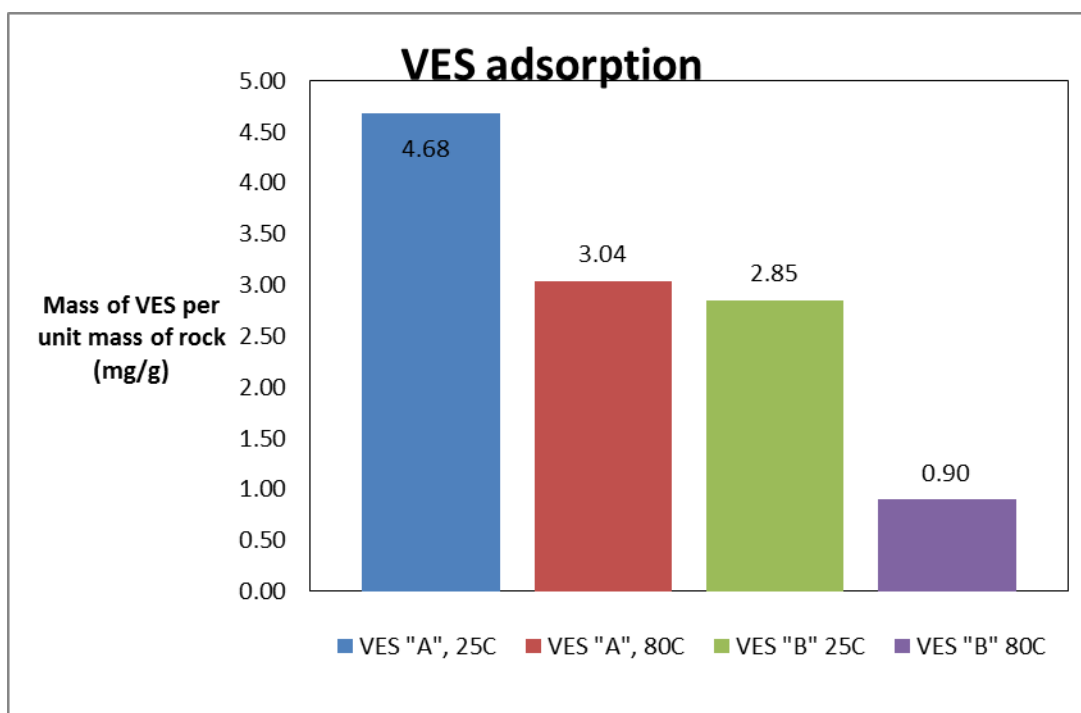


Fig.-2.5 VES "A" and "B" adsorb on the Austin Cream Chalk rock surface at 25 and 80°C

Fig. 2.5 suggests that VES "A" adsorbs more than VES "B" at 25 and 80°C. For both VES formulations, increasing temperature reduced the amount of VES adsorption with the reduction being more significant with VES "B". This suggests that the decrease in VES adsorption due to temperature increase was more significant than the increase in adsorption due to precipitation of VES from the spent acid solution.

2.4 Section 2 conclusions

We have demonstrated using the two-phase titration experiment that VES "A" and "B" adsorb on the surface of Austin Cream Chalk at 25 and 80°C. Surfactant adsorption can change wettability. Wettability changes observed in contact angle experiments in Sections 3 and 4 can be attributed to VES adsorption. .

3 NEW PROCEDURE FOR CONTACT ANGLE EXPERIMENTS

In Section 2, we showed that VES “A” and “B” adsorb on Austin Cream Chalk rock surfaces at 25 and 80°C. In this Section, we studied the effect of VES adsorption on wettability.

From our literature review, surfactant wettability studies use contact angle measurements that represent advancing contact angles. However, wettability during stimulation is represented by receding contact angles.

Therefore, we applied the procedure for conventional static receding contact angle experiments to study the effect of spent acid solutions with HCl only, spent acid solutions with HCl and VES “A” only, and spent acid solutions with HCl, VES “A” and EGMBE on wettability.

We demonstrate using spreading coefficient calculations that results of static receding contact angles may be misinterpreted as strongly oil-wet if low oil-acid IFT's cause oil droplets to spread. Spreading could be a reflection of the effect of the surfactants on the fluid-fluid interface rather than the rock-fluid interface.

We developed a new procedure that ensures that our results reflect the effect of VES adsorption or an EGMBE preflush and postflush on the rock-fluid interface while excluding artifacts caused by fluid-fluid interactions. The new procedure can be applied to dynamic contact angle experiments like the DDDC technique (Rao and Girard, 1996) that use static receding contact angles.

We used the new procedure to study the effect of spent acid solutions with VES “A” and EGMBE, representative of mixing after an acid treatment, on wettability. Lungwitz et al (2007) found that spent acid solutions with VES only were water-wetting, and that spent acid solution with VES and EGMBE were strongly water-wetting.

We found that spent acid solutions with VES “A” and EGMBE, made Austin Cream Chalk rocks to water-wet. Spent acid with VES “A” only was strongly oil-wetting initially.

3.1 Literature review

In this Section, we define sessile-drop, and advancing and receding contact angle measurements. We also reviewed papers on wettability studies. Many papers studied the effect of surfactants used in enhanced oil recovery (EOR) on wettability using imbibition and relative permeability experiments. For wettability studies using contact angle experiments, sessile-drop contact angle experiments with oil droplets on top of rock samples were the most common.

3.1.1 Sessile drop contact angles

Sessile drop contact angles are measured in two ways (Tiab and Donaldson, 1996). An oil-droplet is placed on top of a rock sample lying flat in the solution whose effect on wettability is to be studied. The oil droplet can also be placed beneath the flat surface of the rock in the solution whose effect on wettability is to be studied. In our study, we measured sessile drop contact angles with oil droplets beneath the surface of the rock.

3.1.2 Advancing and receding contact angles

Contact angles measured between oil and a rock could be either advancing or receding (Rao and Girard, 1996).

The wettability obtained from advancing contact angles is representative of a waterflood. In a waterflood, a water-based fluid displaces oil. Therefore advancing contact angles measured to simulate the flow of water as it advances over a piece of rock that formerly had oil adhered to it are representative of wettability in a waterflood (Rao, 1999; Rao, 2003).

The wettability obtained from receding contact angles is representative of a stimulation treatment. When reservoir fluids are produced after a stimulation treatment, oil displaces a water-based fluid. Therefore, receding contact angles measured to simulate the flow of oil as it advances over a piece of rock that formerly had water adhered to it are representative of wettability in stimulation.

In our sessile-drop static contact angle experiments with an oil droplet below the rock, an oil droplet is released from a capillary needle onto a rock surface immersed in a spent acid solution and must displace spent acid before adhering to the rock. This is therefore a receding contact angle and is representative of wettability in stimulation.

In contrast, static sessile drop contact angle experiments with the oil droplet above the crystal represent advancing contact angles because the displacement of the oil droplet requires water to advance over a portion of the crystal covered with oil.

The DDDC technique was developed by (Rao and Girard, 1996) for measuring dynamic advancing and receding contact angles simultaneously. It involves measuring

static receding contact angles with an oil droplet beneath two rock samples, and then turning one of the rocks upside down and merging the droplets. The lower rock sample is then shifted sideways and the advancing and receding contact angles are measured when the three-phase contact line moves.

3.1.3 Stimulation studies related to wettability

Berea formation outcrop cores saturated with fracturing fluids containing a water-wetting surfactant showed a higher hydrocarbon permeability than cores saturated with fracturing fluids containing an oil-wetting surfactant (Jennings and Alfred, 1975).

Lab and field studies showed using capillary pressure measurements show that non-wetting agents that induce a neutral wettability enhance the displacement of stimulation fluids by oil (Penny et al., 1983).

It was recommended that acidizing fluid additives should be selected to create wettability changes that enhance the clean-up of stimulation fluids (Hinkel et al., 2003). In that study, contact angles were determined from imbibition experiments.

The conclusion that can be drawn from this review is that neutral wettability is the preferred wettability in order to produce stimulation fluids. On the other hand, water-wetness is required to maximize oil production after the spent acid has been displaced.

In addition, rock-fluid and fluid-fluid interactions are equally important for displacing stimulation fluids such as spent acid and fracturing fluids. However, after stimulation fluids are displaced, the rock-fluid interaction affects the production of hydrocarbons.

3.1.4 EOR studies related to wettability

In some EOR wettability studies, distinctions were made between surfactants that reduce the oil-acid IFT and surfactants that change the wettability (rock-fluid interface) of the rock (Ayirala and Rao, 2004). Surfactants were shown to cause wettability changes (Sanchez and Hazlett, 1992) by adsorption and surface tension reduction. In both studies, wettability alterations were inferred from relative permeability curves.

Cationic surfactants were shown to alter the wettability of chalk from spontaneous imbibition experiments (Standnes and Austad, 2000b). A surfactant was also shown to alter the wettability of glass plates in wilhemmy plate contact angle experiments to water-wet by Schramm and Mannhardt (1996).

Ayirala et al. (2006) studied the effect of surfactant adsorption on dolomite crystals by observing the effect of injected surfactant solutions on oil droplets between two crystal surfaces during surfactant injection. There was repulsion between surfactant molecules adsorbed on the rock and injected oil droplets, and a detachment of previously adhered oil droplets due to surfactant adsorption at the rock-fluid interface. The DDDC technique (Rao and Girard, 1996) for contact angle experiments was used to measure advancing and receding contact angles as surfactants were injected into the optical cell. However, surfactants were shown to significantly reduce the oil-brine IFT. Therefore, the receding contact angles could have been affected by fluid-fluid interactions. The wettability was inferred from capillary forces that consisted of IFT and advancing contact angle measurements.

Mohan et al. (2011) showed that sessile drop contact angles of oil droplets on calcite plates were altered by surfactant adsorption. Similarly, other studies of the effect of surfactants on wettability included observing the effect of surfactant injection on the contact angle of a sessile oil droplet on a crystal (Standnes and Austad, 2003b; Hirasaki and Zhang, 2004; Seethepalli et al., 2004; Zhang Leslie et al., 2006). The results of these experiments represent advancing contact angles, because to displace oil droplets the surfactant solution advances over crystal/rock surfaces previously covered by oil.

Xu et al. (2008) studied the effect of surfactant injection on the contact angle of oil droplets between two crystals. The contact angles measured on the lower crystal surface were advancing and receding contact angles. The contact angles on the upper crystal surface were receding contact angles. Their measurements showed that surfactants reduced the oil-brine IFT. Therefore, the receding contact angles could have been affected by fluid-fluid interactions.

3.1.5 Section 3.1 summary

From our literature review, surfactant wettability studies use sessile-drop contact angle experiments with oil droplets on the rock that represent advancing contact angles. However, wettability in stimulation is represented by receding contact angles.

Receding contact angles were measured, but in solutions in which surfactants reduced the oil-brine IFT.

From our experiments and analysis (below), the results of receding contact angles may be misinterpreted if low oil-acid IFT's cause oil droplets to spread. Spreading could be a reflection of the effect of the surfactants on the fluid-fluid interface

rather than the rock-fluid interface. A procedure that shows the effect of VES and EGMBE on the rock-fluid interface only, and so represents the actual wettability, is required.

3.2 Experimental details

3.2.1 Porous media

Austin Cream Chalk rocks were prepared as described in Section 2.1.2.

The water-wet rocks used were from step 2 in Fig. 2.2. Oil-wet rocks used were from step 4 in Fig. 2.2.

3.2.2 Fluids

Spent acid solutions with HCl, and HCl and VES were prepared as described in Section 2.1.3.

Continuing from step 6 in Section 2.1.3, spent acid solutions with HCl, VES and EGMBE were prepared as follows:

7. Add 10-vol % of EGMBE and stir with a magnetic stirrer until the solution is uniform.

3.2.3 Contact angle experiments

We measured static receding contact angles using a high-pressure pendant drop tensiometer (**Fig. 3.1**).

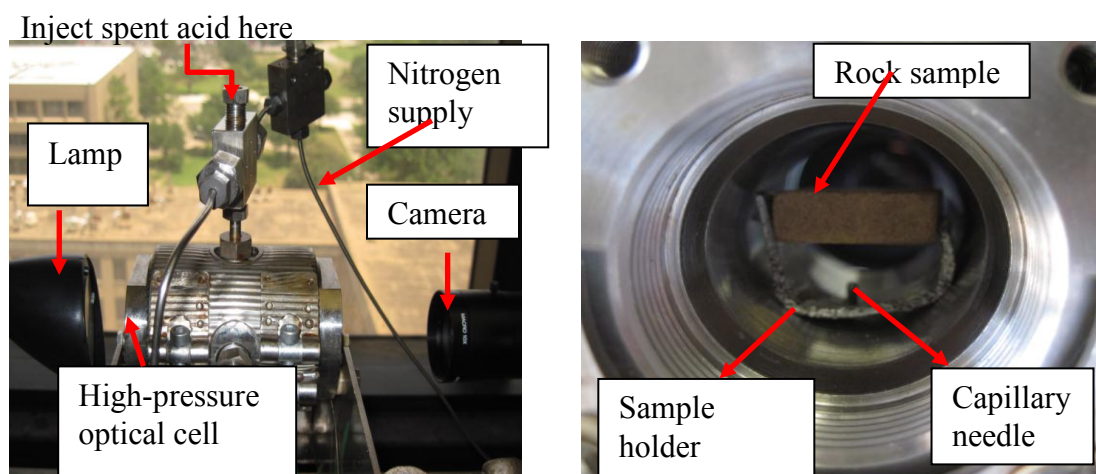


Fig.-3.1 Set-up of pendant drop apparatus for contact angle and IFT measurements.

The major component is the see-through windowed optical cell (Fig. 3.1, left). The maximum operating pressure of the cell is 10,000 psi at a temperature of 200°C. Heat is applied through a heating jacket wrapped around the optical cell and connected to a temperature controller. Pressure was applied from a nitrogen cylinder (Fig. 3.1, left). A lamp illuminates the sample chamber and rock (Fig. 3.1, left). The spent acid is injected through the top port of the optical cell (Fig. 3.1, left). Oil stored in an accumulator is injected through the capillary needle passed through the bottom port of the optical cell (Fig. 3.1, right). The camera (Fig. 3.1, left) captures the image of the oil droplet on the rock surface. A desktop computer was used to store the images from the camera for subsequent analysis. The close up of the optical cell (Fig. 3.1 right) shows the sample holder, rock and capillary needle for injecting oil.

In the conventional procedure for static receding contact angle experiments, the rock is placed on the sample holder, which is placed in the optical cell, and the optical

cell is filled the fluid whose effect on wettability is to be studied. An oil droplet is then injected and forms a sessile drop beneath the rock.

Our objective is to study the effect of spent acid solutions with VES “A” and EGMBE on the wettability (the rock-fluid interface). Therefore, we measured contact angles with rocks with the optical cell filled with:

1. Spent acid solutions with HCl only
2. Spent acid solutions with HCl and VES “A” only
3. Spent acid solutions with HCl, VES “A” and EGMBE

We used the following procedure:

1. Fix the rock sample onto the sample holder; place the sample holder in the optical cell of the high – pressure pendant drop tensiometer. Adjust the sample holder so that the rock rests about 1 cm above the capillary needle (Fig. 3.1, right).
2. Inject the spent acid solution into the optical cell.
3. Apply compressed nitrogen until the optical cell pressure is above the vapor pressure of the spent acid. We used 500 psi for our experiments.
4. Set the temperature controller to the desired temperature.
5. Allow two hours for the temperature to reach equilibrium. This is because wettability is a function of temperature. Injecting oil before the rock temperature is at equilibrium may lead to results that show the rocks to be more oil-wet than they actually are.
6. Turn on the lamp to illuminate the sample.

7. Open the valve leading to the accumulator to inject an oil droplet into the optical cell via the capillary needle below the rock. The droplet rises by buoyancy and spreads or forms a sessile drop on the lower surface of the rock.
8. Capture images using the camera. Spreading oil droplets were captured by setting the camera to take pictures at intervals of 0.04 second.
9. For non-spreading droplets, use drop shape analysis (Río and Neumann, 1997) software to analyze the pendant drop image and calculate the contact angle.
10. At the end of the experiment, clean the sample chamber with xylene to remove the crude oil, and with acetone to remove xylene, and finally with de-ionized water.

The high-pressure pendant drop tensiometer was calibrated for contact angle measurements by measuring the contact angle between sour oil and an un-aged Austin Cream Chalk sample, which was 30° at room temperature (**Fig. 3.2**).

We considered angles between 0° and 80° degrees water-wet. Angles between 80° and 110° are considered intermediate-wet, and angles between 110° and 180° degrees are considered oil-wet(Tiab and Donaldson, 1996).

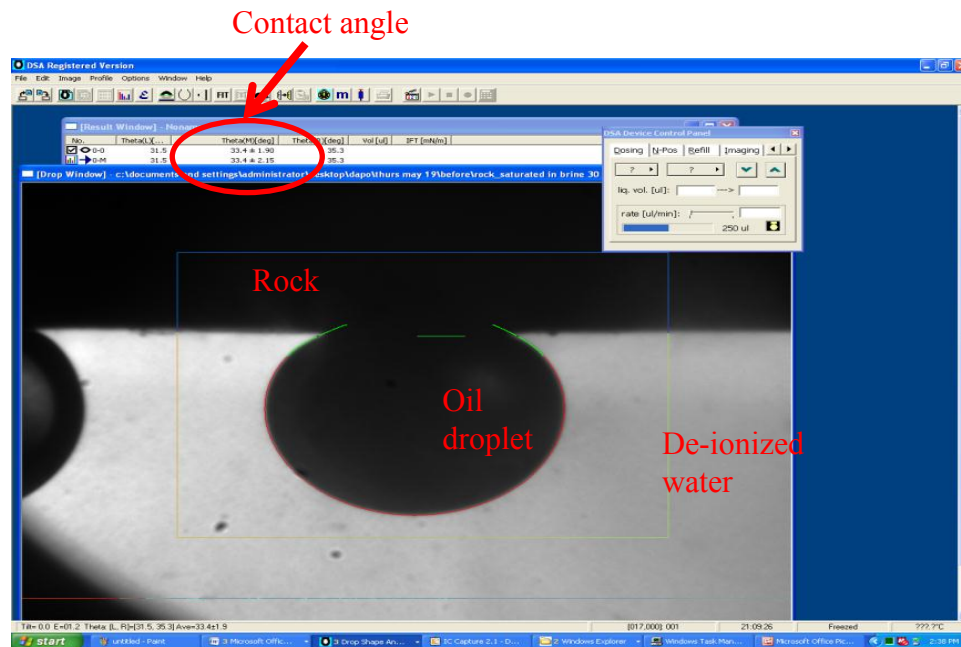


Fig.-3.2 Calibrating the HTHP tensiometer for contact angle measurements

Contact angle experiments have limited reproducibility if sufficient time is not allowed for the oil droplet to age on the surface of the rock. Hundreds of hours are required for the oil droplet to reach equilibrium with the rock (Anderson, 1986; Rao and Girard, 1996). In addition, contact angle experiments cannot take into account the roughness, heterogeneity, and complex geometry of the rock. Rocks are heterogeneous so pure crystals cannot be representative samples.

In our study, we overcame this problem by preparing rocks to simulate reservoir conditions by ageing the rocks in crude oil (Section 2.1.2). In addition, by storing the rocks in a crude oil jar, we ensured that the rock was at equilibrium with the oil before the experiment.

Acid pumping schedules usually last for a few hours (Economides and Nolte, 2000). Therefore, we monitored final contact angles for 24 to 48 hours for our simulated acid treatments.

3.2.4 IFT measurements

We used a spinning drop tensiometer (**Fig. 3.3**) to measure IFT's between oil and spent acid solutions with VES and EGMBE.

We measured IFT's between oil and spent acid solutions with HCl only with the high-pressure pendant drop tensiometer (Fig. 3.1). We used the Drop shape analysis software to analyze the drop images and calculate IFT's.



Fig.-3.3 The spinning drop tensiometer was used to measure oil-acid IFT's

The spinning drop tensiometer was calibrated by measuring the IFT between a drop of butanol and butanol-saturated water and compared them to the correct value of 1.8 mN/m at 27 °C (Cayias et al., 1975).

IFT's were calculated from measurements of the width of oil droplets viewed through the microscope of the spinning drop tensiometer. We used the following equation from Gardner and Hayes (Undated) to calculate the IFT from the width of the oil droplet.

$$\gamma_{ow}(mN/m) = 0.524 \times 10^9 \times \frac{(\Delta\rho \times \frac{d}{10,000})^3}{P^2} \dots\dots\dots (3.1)$$

In Eqn. 3.1, $\Delta\rho$ is the density difference between fluids in g/cm³, d is the width of the droplet observed through the microscope in 0.1th of an mm, and P is the speed of rotation in revolutions per minute.

3.2.5 Density measurements

An Anton Paar digital density meter was used to measure spent acid and oil densities. Density data is required by DSA software for IFT calculations. The results for oil and spent acid are shown in **Table 3.1**.

Table 3.1 Density (g/cm ³) of oil, and spent acid measured with the density meter				
Temperature (°C)	Spent acid with HCl only	Oil	1 vol % VES "A" only	1 vol % VES "A" & 10 vol. % EGMBE
25	1.255	0.8347	1.2582	1.2584
80	1.2243	0.7940	1.2250	1.2256


3.3 Conventional procedure for receding contact angle experiments

For conventional static receding contact angle experiments, the effect of a fluid on wettability is studied by measuring the contact angle between an oil droplet and the rock surface in the fluid whose effect on wettability is to be studied, with the oil droplet beneath the rock.

In this Section, we applied the conventional procedure to study in the effect of spent acid solutions with HCl only (Section 3.3.1), spent acid solutions with VES “A” only (Section 3.3.2), and spent acid solutions with VES “A” and EGMBE (Section 3.3.2) on wettability.

3.3.1 Effect of spent acid with HCl only

Wettability changed from oil-wet to water-wet as temperature increased for rocks in spent acid solutions with HCl only (**Table 3.2**).

Table 3.2 Wettability tends to water-wet as temperature increases in spent acid solutions with HCl only (see Fig. 3.4) as shown by a decrease in contact angles		
Temperature (°C)	Contact angle ° (Fig. 3.4)	<div style="text-align: center;">  <p>Increasing water-wetness</p> </div>
25	154	
50	127	
80	108	
110	54	

Contact angles decreased from 154° to 54° as temperature increased from at 25 to 110°C (Table 3.2). The contact angle was 154° at 25°C , and decreased to 127° at 50°C , 108° at 80°C , and 54° at 110°C (**Fig. 3.4**). All contact angles were obtained from DSA software analysis.

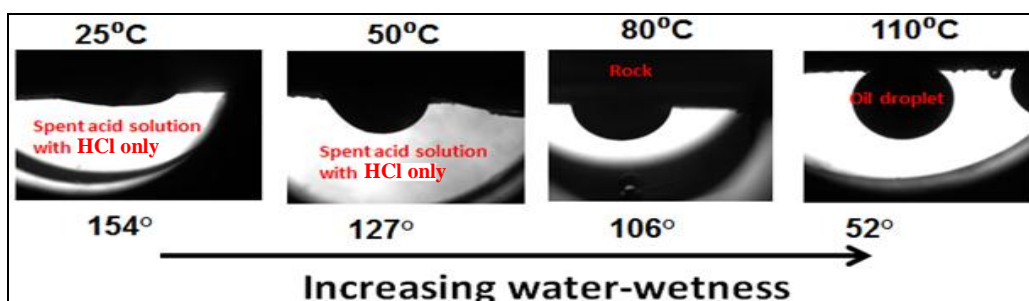


Fig.-3.4 Wettability tended towards water-wet as temperature increased in spent acid solutions with HCl only

The tendency for carbonates to become more water-wet as temperature increases was reported by Rao (1999), Tiab and Donaldson (1996), Wang and Gupta (1995). Hjelmeland and Larrondo (1986) concluded that this may be due to the decrease in the surface activity of surfactants in oil as the temperature increases. Our oil-acid IFT measurements (Section 3.4.2) are consistent with this.

3.3.2 Effect of spent acid with VES “A” and EGMBE on wettability

Oil droplets spread on the surface of Austin Cream Chalk in spent acid solutions with VES and EGMBE. From our literature review, spreading of oil droplets during receding contact angle experiments was interpreted as an indication of strong oil-wet (Rao, 1999).

Oil droplets spread in spent acid solutions 1-vol % VES and 1-vol% EGMBE at 25°C over a time interval of 3 seconds (**Fig. 3.5**).

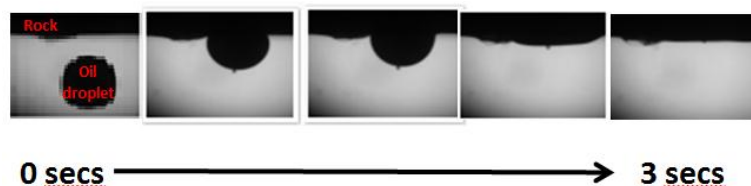


Fig.-3.5 An oil droplet spreads on Austin Cream Chalk in a spent acid solution with 1 vol % VES and 1 vol % EGMBE

Oil spread in spent acid solutions with 1, 2, 3 4 and 6 vol% VES at 25°C.

Typically, droplets spread completely within 5-10 seconds. Oil droplets also spread in spent acid solutions 1% vol VES at 110°C and in spent acid solutions with 1 vol% VES and 10-vol % EGMBE at 110°C.

These results are in contrast with the results in Section 3.3.1 for spent acid solutions with HCl only, in which wettability changed from oil-wet to water-wet as temperature increased.

3.3.3 Section 3.3 conclusion

From Sections 3.3.2 and 3.3.3, we can conclude that the effect of spent acid with HCl only is to change wettability from oil-wet to water-wet as temperature increases from 25 to 110°C. The effect of spent acid with VES and EGMBE is to make rocks strongly oil-wet over the same temperature range.

The results in Section 3.3 are summarized in **Table 3.3**.

Table 3.3 Results for contact angle experiments using the conventional procedure				
Temperature (°C)	VES (Vol %)	EGMBE (vol %)	Contact Angle (°)	Wettability
25	1,2,3,4,6	0	Spreading	Strongly oil-wet?
25	1	1,5	Spreading (Fig. 3.5)	Strongly oil-wet?
60	3	0	Spreading	Strongly oil-wet?
80	1	0	Spreading	Strongly oil-wet?
110	1	0	Spreading	Strongly oil-wet?
110	1	5,10	Spreading	Strongly oil-wet?
25, 50, 80, 110	No VES	No EGMBE	50 to 160 (Fig. 3.4)	Water-wet to oil-wet

In Section 3.4, we shall see that this interpretation is not correct. The results of static receding contact angle experiments with an oil droplet beneath the rock surface are distorted by low oil-acid IFT's.

3.4 Drawback of conventional procedure

In this Section, we showed using spreading coefficient calculations that spreading of oil droplets could be because of changes at the fluid-fluid interface, rather than the rock-fluid interface when oil-acid IFT's are significantly reduced. Therefore spreading may not reflect the wettability of the rock.

3.4.1 Young's equation

Young's equation expresses the relationship between contact angles and the interfacial tensions at equilibrium (Rao and Girard, 1996). It is given by:

$$\cos \theta_{ow} = \frac{\gamma_{os} - \gamma_{ws}}{\gamma_{ow}} \dots\dots\dots (3.2)$$

Eqn. 3.2 shows that the receding contact angle, θ_{ow} , is the resultant of three interfacial tensions as shown in **Fig. 3.6**.

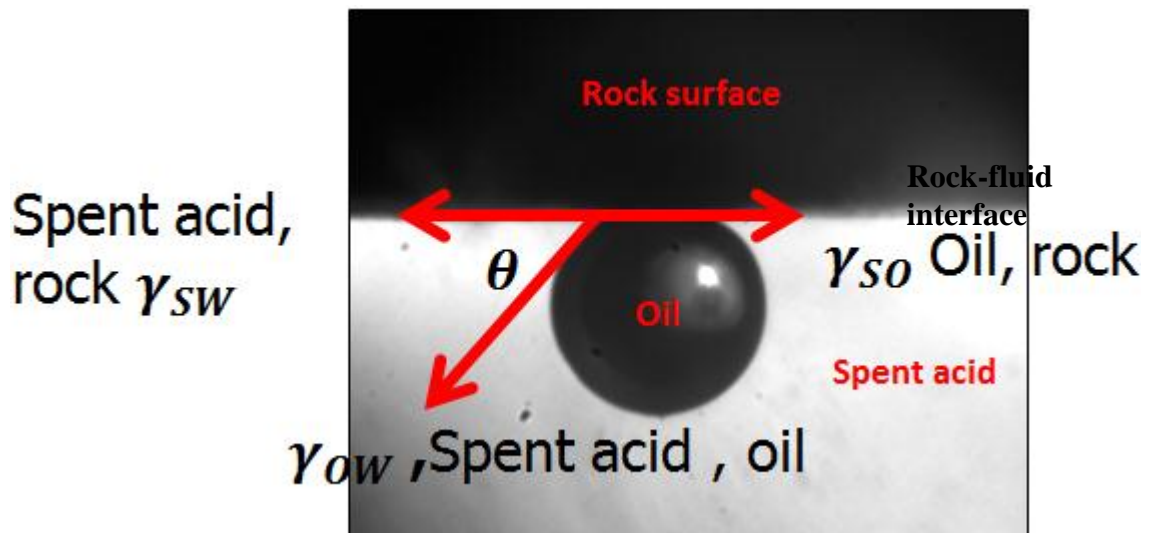


Fig.-3.6 The contact angle is the resultant of IFT's at the rock-fluid interface

The oil-rock interfacial tension (γ_{os}), and the rock-spent acid interfacial tension (γ_{ws}), are at the rock fluid interface (Fig. 3.6). The oil-water interfacial tension (γ_{ow}) is at the oil-spent acid interface (Fig. 3.6).

Fig. 3.6 and Eqn. 3.2 show that contact angles are affected by rock-fluid and fluid-fluid interactions. From Table 3.3, oil droplets spread when experiments were conducted in spent acid solutions with VES “A” and EGMBE. The objective of our study is to know the effect of VES and EGMBE on the rock fluid interface. Therefore, when droplets spread, we need to be sure that the spreading results from the effect of VES and EGMBE on the rock-fluid interface, rather than their effect of the fluid-fluid interface.

To ascertain the effect of VES and EGMBE on spreading in our static receding contact angle experiments, we measured the IFT between oil and spent acid solutions

with VES “A” and EGMBE. Then we compared spreading coefficients for spent acid solutions with HCl only, HCl and VES only, and HCl, VES, and EGMBE.

3.4.2 Spent acid solutions with VES “A” and EGMBE reduce the oil-acid IFT

We measured oil-acid IFT's for spent acid solutions with HCl only, HCl and 1-vol % VES “A” only and HCl, 1-vol % VES “A” and 10-vol % EGMBE at 25 and 80°C.

The average oil acid IFT for spent acid solutions with HCl only was 24.5 mN/m.

The DSA screenshot is shown in **Fig. 3.7**.

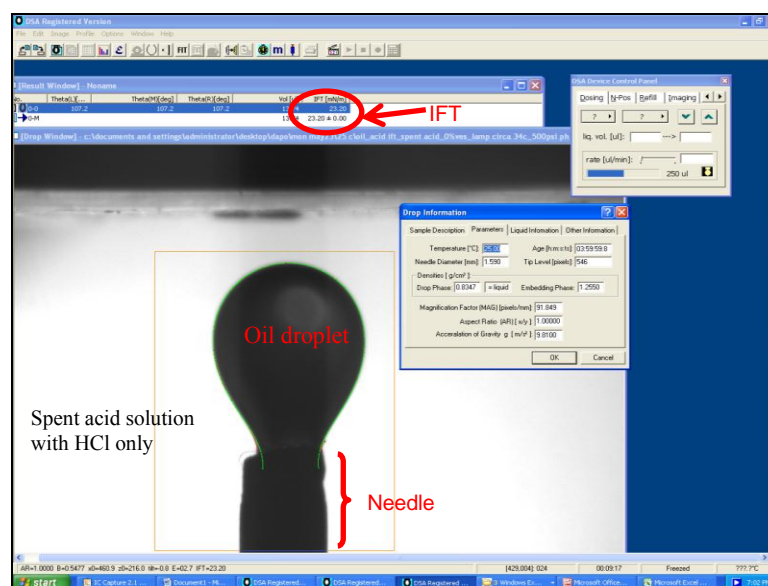


Fig. 3.7 The Oil-spent acid IFT was 24.5 mN/m (circled) in a spent acid solution with HCl only at 25°C

From spinning drop tensiometer measurements, the oil-spent acid IFT for 1-vol % VES “A” only at 25°C was 0.16 mN/m, and the oil-acid IFT for spent acid solutions with 1-vol% VES “A” and 10-vol% EGMBE was 0.75 mN/m (**Fig. 3.8**). Spent acid solutions with VES “A” and EGMBE reduce the oil-acid by 1 to 3 orders of magnitude.

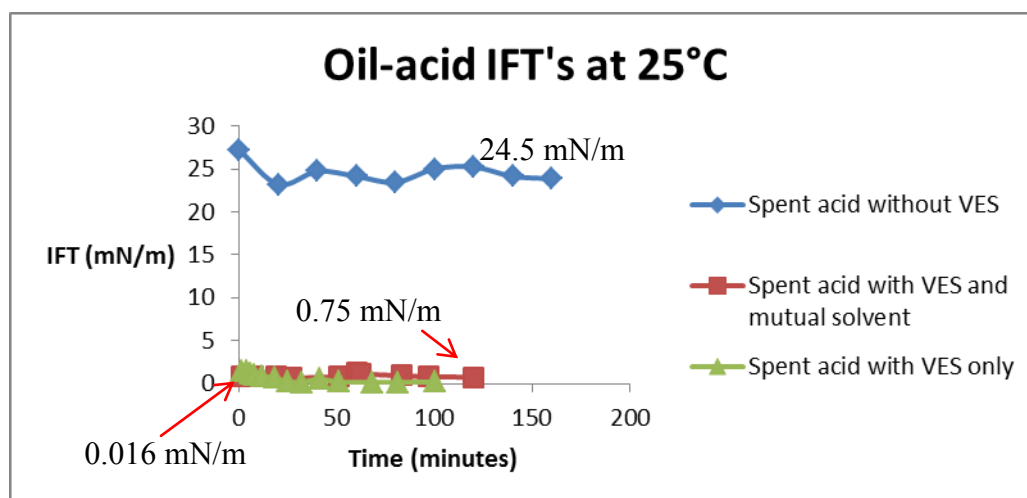


Fig.-3.8 Spent acid solutions with VES and EGMBE significantly reduce oil-spent acid IFT's (VES: 1 vol%, EGMBE 10 vol %)

Similar results were obtained at 80°C (**Fig. 3.9**). The oil-IFT value for spent acid solutions with HCl was 27 mN/m. The oil-acid IFT for spent acid solutions with VES and EGMBE was 3 mN/m and the IFT between oil and spent acid with VES only was 0.04 mN/m (Fig. 3.9).

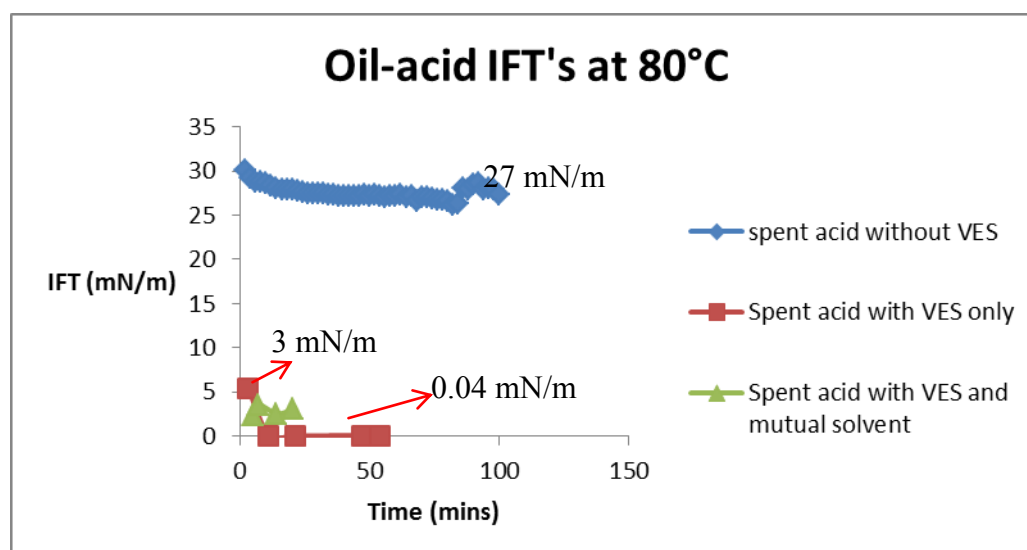


Fig.-3.9 Spent acid solutions with VES and EGMBE significantly reduce oil-spent acid IFT's compared with spent acid solutions with HCl only at 80°C (VES: 1 vol%, EGMBE 10 vol %)

IFT measurements show that spent acid solutions with VES “A” and EGMBE significantly reduce the oil-acid IFT compared with spent acid solutions with HCl only. EGMBE reduces the surface activity of VES at the oil-acid interface.

Increasing the temperature from 25 to 80°C increases the oil-acid IFT from 0.016 mN/m to 0.04 mN/m (Figs. 3.8, and 3.9) for spent acid solutions with 1-vol % VES “A” only. This reduction in surface activity of VES “A” as temperature increases is consistent with the reduction in VES adsorption with increasing temperature in Section 2.

The addition of EGMBE to spent acids solutions with VES only increased the IFT from 0.04 to 3 mN/m at 80°C (Fig. 3.9) and from 0.016 to 0.75 mN/m at 25°C (Fig. 3.8). This suggests that EGMBE reduces the surface activity of the VES. The reduction in surface activity of solvents by EGMBE has been reported (Hall, 1975; Economides and Nolte, 2000).

3.4.3 Spreading coefficients explain why oil droplets spread

The spreading observed in spent acid solutions with VES and EGMBE can be explained by Rao’s (1999) plot of contact angle against IFT. The plot shows that there is a minimum oil-brine IFT below which oil droplets will spread on the surface of the rock.

The oil-brine IFT below which oil droplets will spread is called the critical spreading tension. The spreading of oil droplets affects the distribution of fluids in the reservoir, therefore, spreading coefficients are of interest in enhanced oil recovery studies (Oren and Pinczewski, 1994; Mani and Mohanty, 1997; Ghannam, 2003).

To the best of our knowledge spreading coefficients have not been applied to the study of the results of contact angle experiments. In our study, we applied spreading coefficients to show that oil droplets can spread even when rocks are intermediate -wet – therefore, the contact angles would not reflect the rock-fluid interaction.

The spreading coefficient is defined for a liquid-liquid-gas system as the difference between the force of adhesion between the spreading liquid and the second liquid, and the force of cohesion within the spreading liquid (Harkins and Feldman, 1922). The spreading coefficient for an oil droplet on a rock surface in a spent acid solution (a solid-liquid-liquid system) is the difference between the forces of adhesion between the oil and the rock, and cohesion within the oil droplet.

Increasingly positive oil spreading coefficients indicate that the oil droplet will tend to spread on the rock surface. The oil tends to form droplets with an increasing contact angle until it spreads on the surface of the rock when the spreading coefficient is zero and the contact angle is 180° . An increasingly negative oil-spreading coefficient indicates that the oil droplet is less likely to spread because adhesion of oil for the rock surface is less than cohesion between the oil molecules. It follows that the contact angle of the oil droplet decreases as the spreading coefficient decreases.

From Tiab & Donaldson (1996), the spreading coefficient for oil on a rock in a spent acid solution can be expressed as:

$$S_{os} = \gamma_{ws} - \gamma_{os} - \gamma_{ow} \dots\dots\dots (3.3)$$

In **Eqn. 3.3**, γ_{ws} , γ_{os} , and γ_{ow} are as described in Fig. 3.6. Eqn. 3.3 cannot be used to calculate the spreading coefficient because γ_{ws} and γ_{os} cannot be measured directly experimentally.

However, Young's equation (Eqn. 3.2) applies for non-spreading oil droplets. Therefore, substituting the difference in the rock-fluid interfacial tensions ($\gamma_{ws} - \gamma_{os}$) into Eqn. 3.3, the spreading coefficient can be expressed for non-spreading oil droplets as:

$$S_{os} = -\gamma_{ow} \times (\cos \theta_{ow} + 1) \dots\dots\dots (3.4)$$

From **Eqn. 3.4**, the spreading coefficient for an oil-droplet at 80°C (Contact angle = 106°, Fig. 3.4, IFT = 27 mN/m, Fig 3.9) in a spent acid solution with HCl only is -19.5 mN/m (**Table 3.4**). This is consistent with the oil droplet forming a sessile drop beneath the intermediate-wet rock surface (Fig. 3.4)

For spreading oil droplets, Eqn. 3.4 cannot be applied, and the spreading coefficient cannot be calculated. However, we can demonstrate the effect of VES and EGMBE on spreading by assuming that the rock-fluid interfacial tensions are unchanged by spent acid with VES and EGMBE at 80°C (i.e. the rock surface remains intermediate-wet).

Substituting the IFT of 27 mN/m and the spreading coefficient of -19.5 mN/m, into Eqn. 3.3, the difference in rock-fluid interfacial tensions, " $\gamma_{ws} - \gamma_{os}$ " = 7.5 mN/m.

From Fig. 3.9, the oil-acid IFT, γ_{ow} , is reduced from 27 mN/m in spent acid with HCl only to 3 mN/m in spent acid with HCl, 1-vol % VES and 10-vol% EGMBE. Therefore, substituting for " γ_{ow} " and " $\gamma_{ws} - \gamma_{os}$ " in Eqn. 3.3, the spreading

coefficient for the spreading oil droplets is “ $7.5-3=4.5$ ” mN/m (Table 3.4). This positive spreading coefficient is consistent with the oil-droplets spreading on the surface of the rock (Fig. 3.5).

Table 3.4 Spreading coefficients show that oil droplets do not spread on rocks in spent acid solutions with HCl only, but spread in spent acid solution with VES and EGMBE at 80°C		
Spent acid solution	Oil of Spreading coefficient (mN/m)	Remarks
0 vol% VES,	-19.5 (Eqn. 3.4)	Oil does not spread (Fig. 3.4)
1 vol% VES + 10 vol% EGMBE	4.5 (Eqn. 3.5)	Oil spreads (Fig. 3.5)

This analysis in Table 3.4 suggests that oil droplets can spread on the surface of the rock when the oil –acid IFT is low, suggesting that the rock surface is strongly oil-wet, whereas, the rock was intermediate-wet. In that case, the spreading is the effect of VES and EGMBE on the fluid-fluid interface, rather than the rock-fluid interface, and so does not represent the actual wettability.

3.4.4 Section 3.4 summary

Spent acid solutions with VES “A” and EGMBE significantly reduce the IFT between oil and spent acid, compared with spent acid with HCl only.

Spreading coefficient calculations suggest that low oil-acid IFT’s can cause an artifact that can distort the results of static receding contact angle experiments. There is a possibility that if oil-acid IFT’s are low, the oil droplet will spread, and reflect the effect of VES and EGMBE on the fluid-fluid interface, rather than the rock-fluid interface.

This justifies the need for a procedure that reflects the effect of VES and EGMBE on the rock-fluid interface only. This can be achieved by keeping oil-acid IFT’s large and similar for all contact angle experiments.

3.5 New procedure

First, we measured all contact angles in spent acid solutions with HCl only. These solutions have relatively high oil-acid IFT's (Figs. 3.7 and 3.8), while retaining the characteristics of the environment (e.g. pH and salt concentration) in which the rocks wettability was to be studied.

Secondly, the rocks were centrifuged in different spent acid solutions to simulate the flow of spent acid through the pores. Centrifuging the Austin Cream Chalk rocks in different spent acid solutions should cause the surfactants in the spent acid to adsorb onto the surface of the rock.

Since the IFT's of fluids in which contact angles are measured are high, our results reflect the effect of VES adsorption or an EGMBE preflush and postflush on the rock-fluid interface, rather than their effect on the oil-acid interface.

Our literature review and lab experiments suggest that centrifuging Austin Cream Chalk in spent acid solutions with VES and EGMBE can change the wettability of the rock.

Rocks became more oil-wet after ageing in crude oil in our lab (Fig. 2.1, step 4, and **Fig. 3.10**). The wettability of Austin Cream Chalk rock samples changed from water-wet (about $30-45^\circ$) to oil-wet (about 140°) after saturation with formation brine and crude oil and ageing for 60 hours in crude oil.

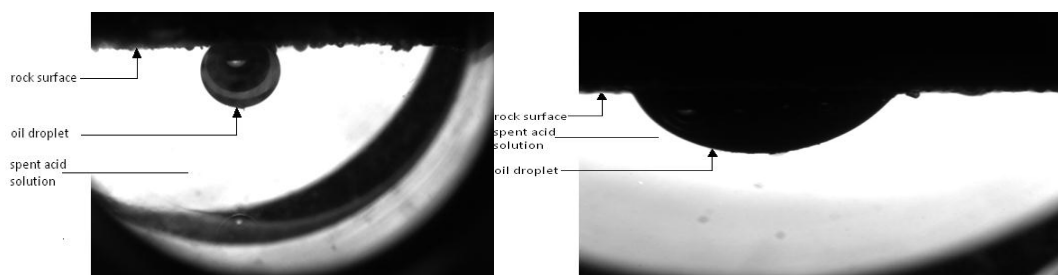


Fig.-3.10 Ageing in crude oil caused change from water-wet ($30-45^\circ$, left) to oil-wet (140°) at 25°C

This showed that the ageing process was effective in simulating the process by which a brine-saturated rock is filled with oil after which the surface-active agents in the oil change the wettability from oil wet to water-wet.

Carboxyl groups and polar compounds in oil have been shown to cause carbonate rocks to become more oil-wet (Lowe et al., 1973; Sayyounh et al., 1991; Tiab and Donaldson, 1996). Wettability alteration, measured using spontaneous imbibition, was accomplished by aging crude oil-saturated chalk cores for different time intervals and at different temperatures (Standnes and Austad, 2000a). Rock wettability determined from Amott test experiments was altered by flowing fluids with oil and water-based drilling muds through the rock (Cuiec, 1989).

Interactions between surfactants and adsorbed carboxylates from crude oil were shown to alter chalk wettability from oil-wet to water-wet (Mohan et al., 2011). Amott, imbibition, and waterflooding experiments showed that the wettability of carbonate and sandstone cores was altered by ageing in crude oil (Graue et al., 1999).

The new procedure for static receding contact angle experiments can be applied to dynamic contact angle experiments like the DDDC technique. The DDDC technique involves measuring static receding contact angles before flipping the crystals to measure

dynamic contact angles. Porous rock samples can be prepared by ageing and saturating them with surfactant solutions. Advancing and receding contact angles can then be measured in a neutral fluid with no surfactants, such as formation brine.

3.6 New procedure: Application to study the effect of VES “A” on wettability

We applied the new procedure for static receding contact angle experiments to study the effect of spent acid solutions with HCl only, with HCl and VES “A” only, and HCl, VES and EGMBE on wettability.

3.6.1 Experimental studies

The procedure for preparing porous media in Section 2 was modified as shown in step 5 of **Fig. 3.11**:

5. The water-wet and oil-wet rock samples were centrifuged at 5,000 rpm for two hours in:
 - a. Spent acid solutions with HCl only,
 - b. Spent acid solution with 1 vol % VES “A” only
 - c. A spent acid solution with 1 vol % VES “A” and 10 vol % EGMBE

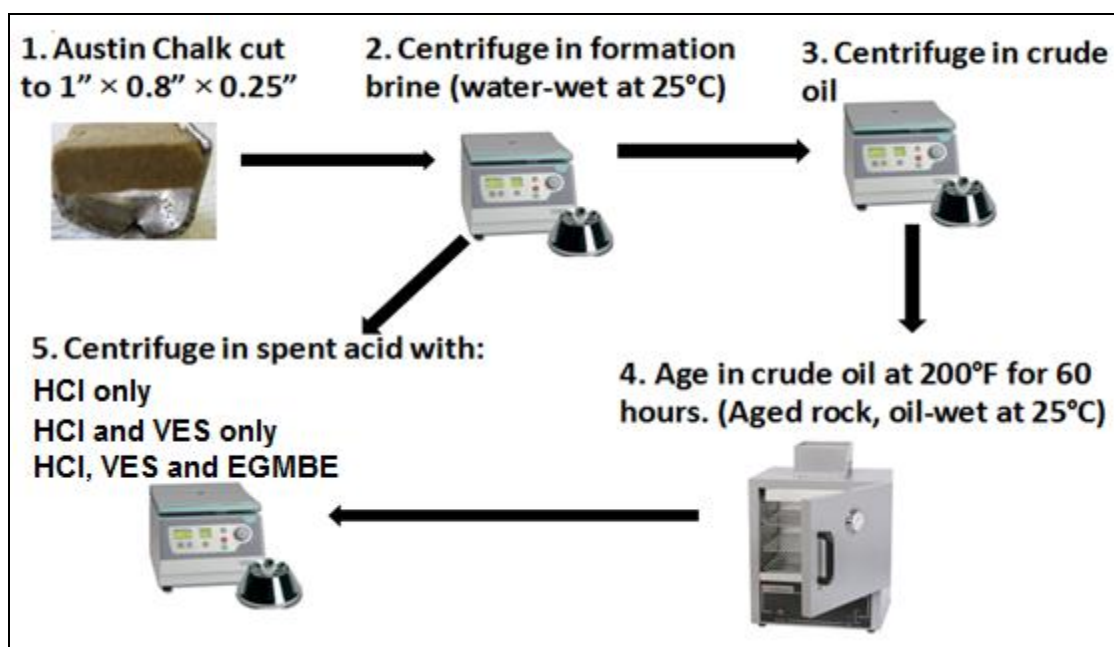


Fig.-3.11 Preparation of porous media to study the effect of spent acid on wettability using the new procedure for contact angle experiments

Step 5 simulates the flow of spent acid through the invaded zone around the reservoir.

The effect of VES adsorption on contact angles was determined by comparing contact angles in spent acid solutions with HCl before and after centrifuging in the three spent acid solutions.

3.6.2 Results

The wettability of a rock centrifuged in a spent acid solution with 1-vol % VES "A" only was changed to strongly oil-wet (3.6.2.1).

The wettability of a rock centrifuged in a spent acid solution with 1-vol% VES and 10-vol% EGMBE changed from oil-wet to water-wet (3.6.2.2).

In the control experiment, the wettability of a rock centrifuged in a spent acid solution without VES did not change (3.6.2.3). The results are summarized in **Table 3.5**.

Table 3.5 Effect of spent acid on wettability (VES = 1-vol %, EGMBE = 10-vol %)			
Spent acid solution	Wettability before centrifuging	Wettability after centrifuging	Comment
HCl and VES only	Water-wet	Strongly oil-wet	Adsorption of VES changes wettability
HCl, VES & EGMBE	Oil-wet	Water-wet	EGMBE makes rocks water-wet
HCl and VES only	Oil-wet	Strongly Oil-wet	Adsorption of VES changes wettability
HCl only	Oil-wet/water-wet	Same as initial	No surface active agents so no change
HCl, VES & EGMBE	Water-wet	Strongly Water-wet	EGMBE makes rocks water-wet and prevents VES adsorption

3.6.2.1 Effect of spent acid solutions with 1 vol% VES “A” only

A water-wet Austin Cream Chalk rock with a contact angle of 33° became strongly oil-wet with the oil droplet spreading on the rock after it was centrifuged at 5,000 rpm for two hours in a spent acid solution with 1-vol % VES only at 25°C (**Fig. 3.12**). The oil droplet spread on the surface of the rock in less than one second in Fig. 3.12.

Similarly, centrifuging an oil-wet rock in a spent acid solution with 1-vol % VES “A” made the rocks strongly oil-wet initially (**Fig. 3.13**).

Strong oil-wetness probably occurs because of electrostatic attraction between the VES’ polar head and the rock, causing the surfactants’ polar tail to face the solution. This result is not consistent with that of Lungwitz et al (2007).

However, in Fig. 3.12, the rock surface after VES adsorption was observed only for a few minutes. In Section 4, rocks that were strongly oil-wet after contact with VES “A” became water-wet after 12 hours, suggesting that the method of adsorption may be more complex than described above. We conclude that VES “A” adsorption on water-wet Austin Cream Chalk makes the rock strongly oil-wet initially.

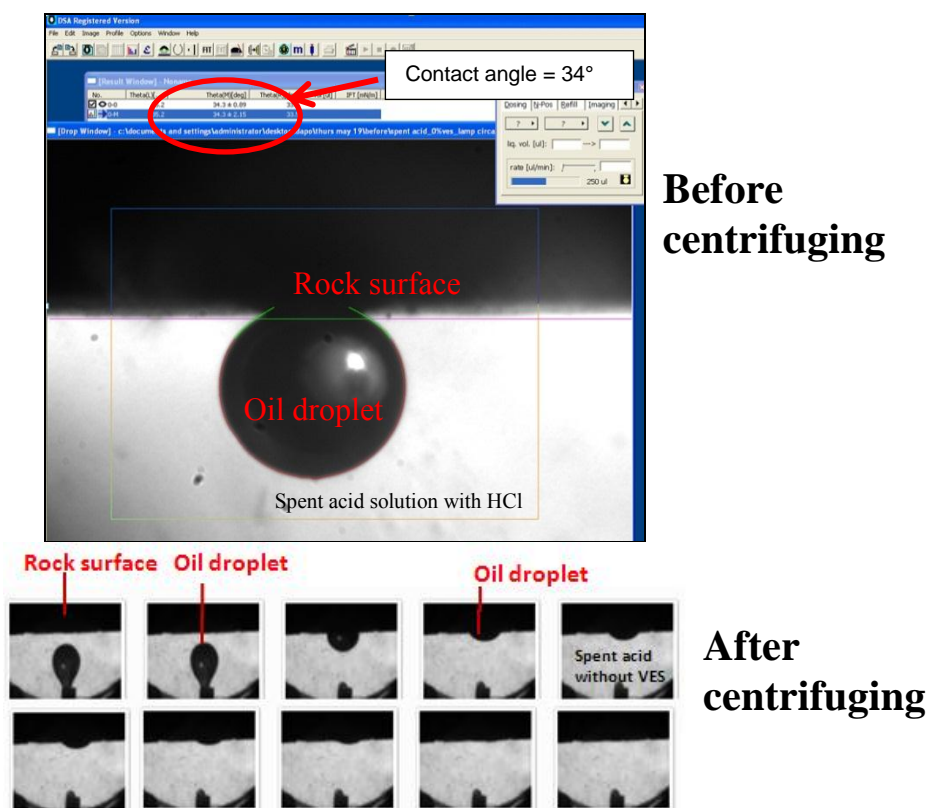
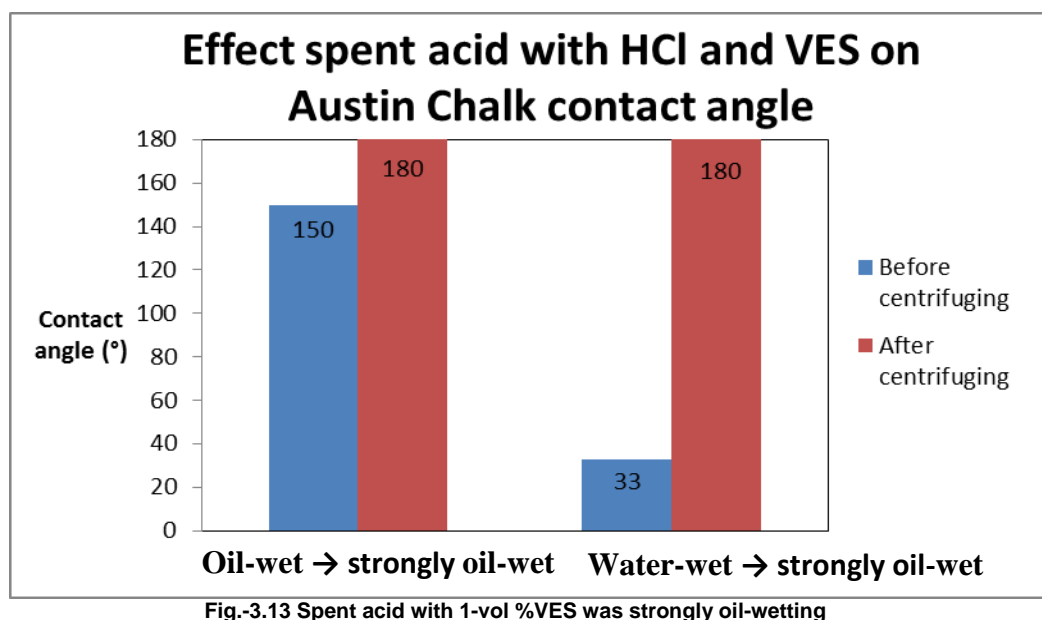


Fig.- 3.12 Centrifuging a water-wet rock in a spent acid solution with 1 vol %VES “A” changed wettability from water-wet (34°, circled top) to strongly oil-wet (bottom)



3.6.2.2 Effect of spent acid solutions with 1 vol % VES and 10 vol% EGMBE

An oil-wet Austin Cream Chalk rock with a contact angle of 155° became water-wet with a contact angle of 41° after it was centrifuged at 5,000 rpm for two hours in a spent acid solution with 1-vol% VES “A” and 10-vol % EGMBE at 25°C (Fig. 3.14).

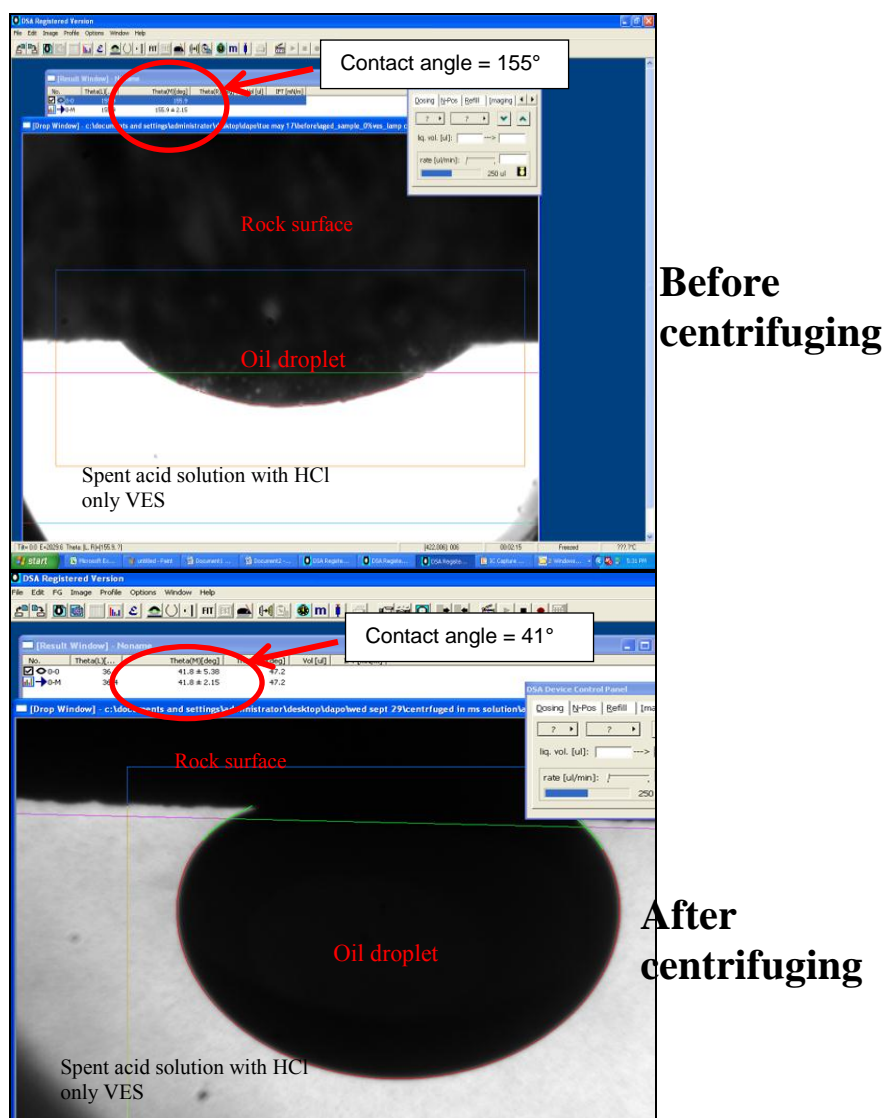


Fig.-3.14 Centrifuging an, oil-wet (top, 155°) rock in a spent acid solution with 1 vol % VES and 10 vol % EGMBE resulted in a change of wettability to water-wet at 41° (circled, bottom right)

Centrifuging a water-wet rock in a spent acid solution with 1-vol % VES and 10-vol % EGMBE resulted in the oil droplet rolling off the surface of the rock. This implies that the rock surface was so strongly water-wet that the oil droplet did not adhere onto the surface of the rock. Thus, we assumed the contact angle was 0° (**Fig. 3.15**).

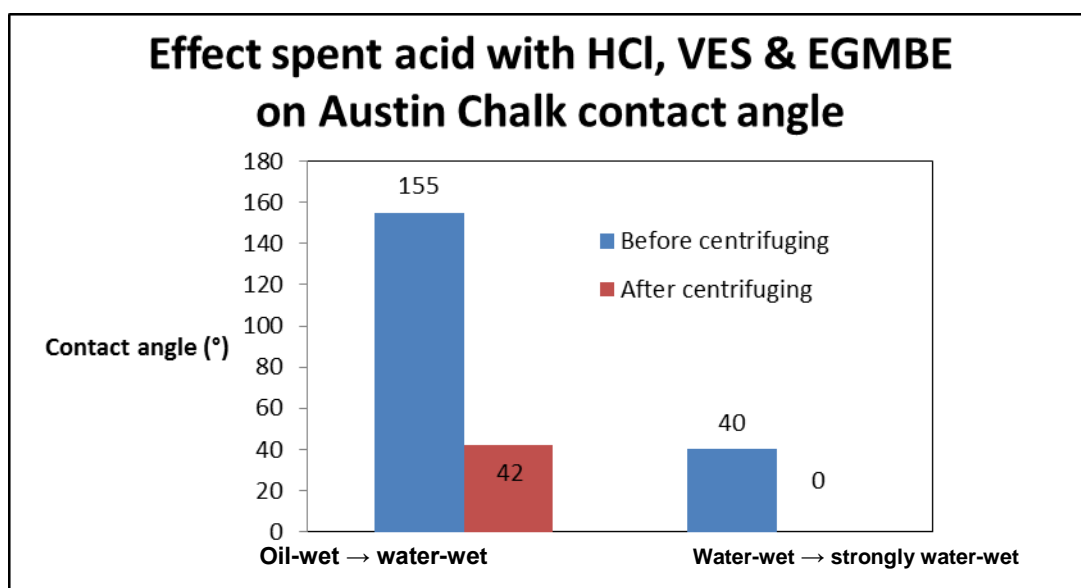


Fig.-3.15 Spent acid with 1-vol% VES and 10-vol% EGMBE was water-wetting

The changes in wettability to water-wetness are consistent with EGMBE's ability to dissolve crude oil components adsorbed on the rock surface (Economides and Nolte, 2000).

The ratio of EGMBE to VES (10:1) in our experiment was greater than the 1:1 ratio used by Lungwitz et al (2007). However, our result is consistent with theirs.

Spent acid solutions with 1-vol % VES only were strongly oil-wetting (Fig. 3.13), whereas, the spent acid solutions with 1-vol % VES and 10-vol % EGMBE were water-wetting (Fig. 3.15). This suggests that 10-vol % EGMBE prevented VES from

adsorbing on the rock-fluid interface. Mutual solvents are known to keep surfactants and other additives in solution, and stop them from adsorbing on the rock interface (Hall, 1975).

3.6.2.3 Effect of spent acid with HCl only

An aged oil-wet Austin Cream Chalk rock remained oil-wet after it was centrifuged at 5,000 rpm for two hours in a spent acid solution with HCl only at 25°C (Fig. 3.16). This was the control experiment.

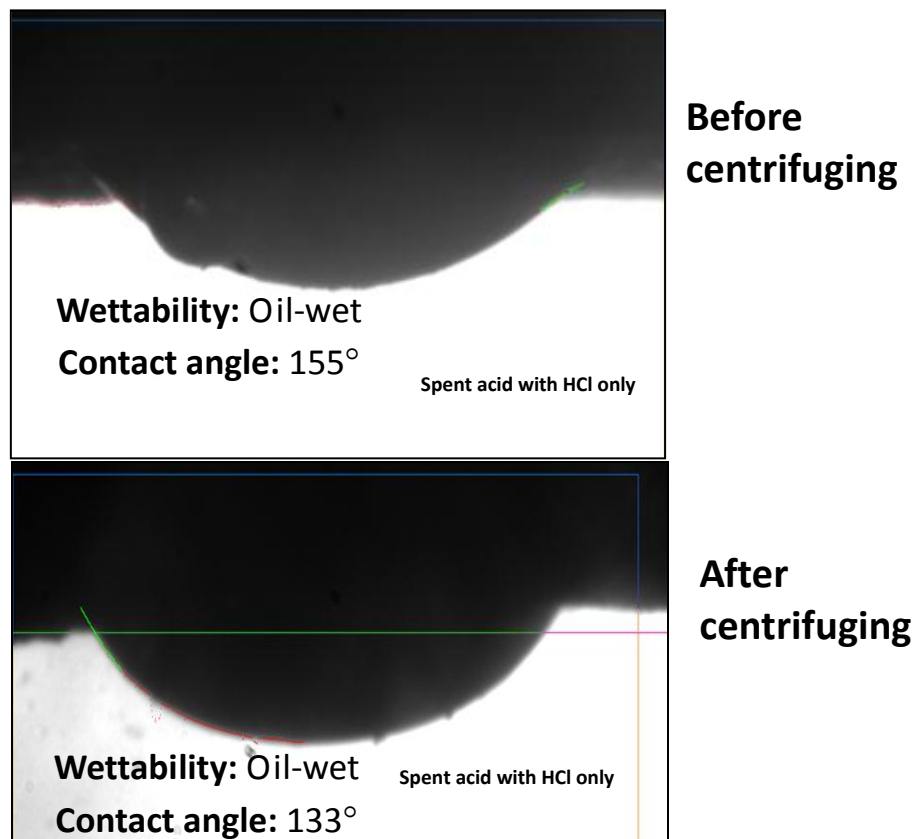


Fig.-3.16 Spent acid with HCl resulted in no change in wettability

Centrifuging a water-wet rock in a spent acid solution with HCl only caused no change in wettability. This is because there are no surface-active agents in spent acid with HCl only (**Fig. 3.17**).

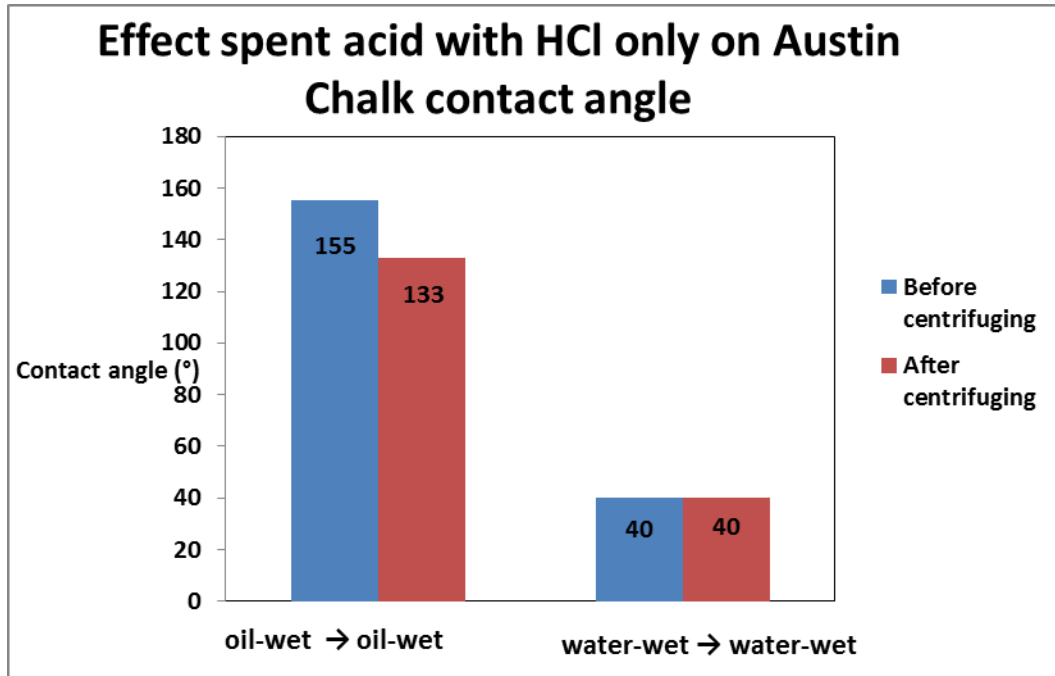


Fig.-3.17 Effect of spent acid with HCl only on contact angle

3.7 Section 3 conclusions

From our literature review, surfactant wettability studies use contact angle measurements that represent advancing contact angles. However, wettability during stimulation is represented by receding contact angles.

Spent acid solutions with VES and EGMBE reduce the IFT between oil and spent acid, relative to spent acid with HCl only. Spreading coefficient calculations show

that the results of conventional receding contact angles may be misinterpreted as strongly oil-wet if low oil-acid IFT's cause oil droplets to spread (Table 3.6).

Table 3.6 Comparison of results (old procedure to new procedure)			
	Conventional procedure (Section 3.3)	New procedure (Section 3.6.2)	
Spent acid solution	Contact angle in spent acid	Initial wettability	Wettability after centrifuging
VES &EGMBE	Strongly oil-wet?	Water-wet	Strongly water-wet
		Oil-wet	Water-wet

Spreading was a reflection of the effect of the surfactants on the fluid-fluid interface rather than the rock-fluid interface. We developed a new procedure shows the effect of VES and EGMBE on the rock-fluid interface only, and so represents the actual wettability (Table 3.6). The new procedure can be applied to dynamic contact angle measurements like the DDDC technique.

The results from our receding contact angle experiments using the new procedure represent the mixing that occurs during flow back. We found that:

1. Spent acid solutions with 1-vol % VES "A" and 10-vol % EGMBE are water-wetting (Fig. 3.15) at 25°C. This is consistent with Lungwitz et al (2007).
2. Spent acid solutions with 1-vol % VES "A" only were strongly oil-wetting (Fig. 3.13). The oil-wetting effect of spent acid solutions with VES "A" only was not consistent with Lungwitz et al (2007) 25°C. However, longer observation (Section 4) shows that VES "A" has a water-wetting effect.

3. Spent acid solutions with HCl only had no effect on wettability at 25°C (Fig. 3.17). This was because there was no surface-active agent in the acid.
4. EGMBE reduces the adsorption of VES at the rock-fluid, and fluid-fluid interface.

4 SIMULATED ACID TREATMENTS

In Section 2, we demonstrated that VES “A” and “B” adsorb on Austin chalk. In Section 3, we developed a new procedure for static receding contact angle experiments that shows the effect of spent acid with VES and EGMBE on wettability.

The experiments in Section 3.6 are representative of mixing after an acid treatment. In practice however, acid treatments are performed with different fluids pumped in stages (Economides and Nolte, 2000). There are alternating treating fluid-diverter sequences.

In this Section, we centrifuged Austin Cream Chalk rocks in fluids used in the preflush, main acid stage, diverting stage, and postflush to simulate matrix-acidizing treatments by the flow of acidizing fluids through the rock.

We applied the same principle as with the new procedure in Section 3.6. We centrifuged the rock in spent acid with VES and EGMBE to simulate acid treatments. We measured contact angles in spent acid solutions with HCl only to eliminate the artifact caused by low oil-acid IFT's. The results represent wettability just as oil starts to displace spent acid.

We studied the effect of VES “A” and “B” on wettability at temperatures from 25 to 110°C, with VES concentrations of 4-6 vol% and an EGMBE concentration of 10 vol%.

We found an EGMBE preflush and postflush made rocks water-wet after VES “A” and “B” diversion stages. Diversion with VES “A” only was water-wetting at 25°C.

An accurate interpretation of results when oil droplets spread requires an estimate of the critical spreading tension.

4.1 Experimental studies

4.1.1 Porous media

Porous media were prepared as described in Section 2.1.2. Studies of carbonate rock wettability have shown them to vary from neutral to oil-wet (Lichaa et al., 1992). A study of 161 carbonate cores from reservoirs ranging from the Middle East to West Texas (Chilingar and Yen, 1983) showed 80% to be oil-wet or strongly oil-wet. Therefore, we used oil-wet rocks at the start of our experiments because they are most representative of carbonate reservoir wettability.

4.1.2 Fluids

Spent acid solutions were prepared from the reaction products of 20 wt% HCl and CaCO_3 as described in Section 2.1.3.

From step 2 in Section 2.1.3, spent acid solutions with EGMBE only were prepared as follows:

1. Add 10-vol % of EGMBE until the pH is between 4 and 5.

4.1.3 Procedure for contact angle measurements

We used the same procedure as described in Section 3.2.3.

4.1.4 Procedure for experiments to simulate acidizing treatments

Our literature review (Chang et al., 2000; Economides and Nolte, 2000; Safwat et al., 2002; Nasr-El-Din et al., 2003; Nasr-El-Din et al., 2004; Al-Mutawa et al., 2005;

Chatriwala et al., 2005; Nasr-El-DinAl-Arnaout et al., 2005; Nasr-El-DinErbil et al., 2005; Shimizu et al., 2005; Nasr-El-Din et al., 2006; Nasr-El-Din et al., 2006a; Nasr-El-Din and Samuel, 2007) indicates that there are four main stages in a carbonate matrix acidizing treatment with VES as a diverting agent.

These are a mutual solvent preflush, a main/spear head acid stage, a diverting stage, and a mutual solvent postflush.

1. The preflush is used to make the rocks water-wet and displace oil from the near-well region. We used spent acid solutions with HCl and 10-vol % EGMBE as the preflush.
2. The spearhead acid creates the initial channels and acts as a spacer between the mutual solvent in the preflush and the VES. The spearhead is the main treating fluid. We used spent acid solutions with HCl only as the main acid stage.
3. The diversion stage is then pumped to plug the high-permeability zones. The spearhead acid is often alternated with the diversion stage. We used spent acid solutions with HCl and 4-6 vol % VES only as the diversion stage.
4. The postflush is used to break VES gels and to make the rock water-wet after the treatment. We used spent acid solutions with HCl and 10-vol % EGMBE as the preflush.

The carbonate matrix acidizing treatments simulated were:

1. Acidizing with HCl and a VES diversion stage only
2. Acidizing with HCl, a VES diversion stage and an EGMBE preflush and postflush.

The experimental procedure is summarized in **Table 4.1**.

Table 4.1 Experiments to simulate matrix acidizing with HCl only, HCl & VES, HCL, VES & EGMBE			
	Spent acid	VES Only	VES & EGMBE
EGMBE Preflush	10-vol % EGMBE		√ X
Treating Fluid	HCl only	√ X	√ X
Diverting stage	1-6 vol % VES only	√ X	√ X
EGMBE postflush	10-vol % EGMBE	√	√ X
X Centrifuge in spent acid for 20 minutes √ Measure contact angles in spent acid with HCl only			

The rock samples were centrifuged at 5,000 rpm for 20 minutes in different solutions to simulate the effect of the flow of the fluids in the four main stages through the rock (Table 4.1).

The contact angle between oil and the rock was measured before and after each stage in spent acid with HCl only to study the effect of the surface-active compounds in the fluids on the wettability of the rock (Table 4.1). Surface-active agents in the imbibed spent acid resulted in changes in wettability.

We allowed two hours before injecting the oil droplet for the temperature of the rock to reach equilibrium in high-temperature experiments. In addition, at the start of centrifuging, the spent acid was at room temperature and the rock is transferred into the spent acid solution for centrifuging while hot.

Contact angles were observed for up to 36 hours for the initial and final wettability, and the wettability after the diversion stage. Other contact angles were observed for an hour.

4.2 Results and discussion

We performed experiments described in Section 4.1 to simulate acid treatments with a VES diversion stage only, and a VES diversion stage with an EGMBE preflush and postflush (**Table 4.2**).

Table 4.2 Experiments performed to simulate acid treatments					
		VES (vol %)			
	Simulated acid treatment	25°C	80°C	110°C	EGMBE (vol %)
1	VES "A" only	4	-	-	0
2	VES "A" only	-	4	-	0
3	VES "B" Only	4	-	-	0
4	VES "B" Only	-	-	6	0
5	VES "A" + EGMBE preflush and postflush	4	-	-	10
6	VES "A" + EGMBE preflush and postflush	-	4	-	10
7	VES "B" + EGMBE preflush and postflush	4	-	-	10
8	VES "B" + EGMBE preflush and postflush	-	-	4	10

Experiments were conducted at 25, 80, and 110°C. We started all experiments with oil-wet rocks with a contact angle in spent acid of 161-165°.

4.2.1 Simulated acid treatments with a VES diversion stage an EGMBE preflush and postflush

Simulated acid treatments with an EGMBE preflush and postflush changed the wettability of rocks from oil-wet to water-wet (**Table 4.3**).

Table 4.3 Simulated acid treatments with a 4 vol% VES and 10 vol% EGMBE preflush and postflush made rocks water-wet				
VES type	VES (vol %)	Temperature (°C)	Initial Wettability (°) (oil-wet)	Final wettability (°) (water-wet)
"A"	4	25	161-165°	50.4°
"A"		80		77.8°
"B"		25		52.3°
"B"		110		46.7°

The experiments performed in this Section are as follows (Table 4.3):

1. Effect of VES "A" at 25°C (4.2.1.1)
2. Effect of VES "A" at 80°C (4.2.1.2)
3. Effect of VES "B" at 25°C (4.2.1.3)
4. Effect of VES "B" at 25°C (4.2.1.3)

4.2.1.1 Diversion with VES "A" only and an EGMBE preflush and postflush at 25°C

A simulated acid treatment with a 4-vol% VES "A" diversion stage and a 10-vol% EGMBE preflush and postflush changed wettability from oil-wet to water-wet at 25°C. All contact angles were measured in spent acid solutions with HCl only.

Initial wettability: The initial rock wettability was oil-wet in spent acid at 163.7° (Fig. 4.1).

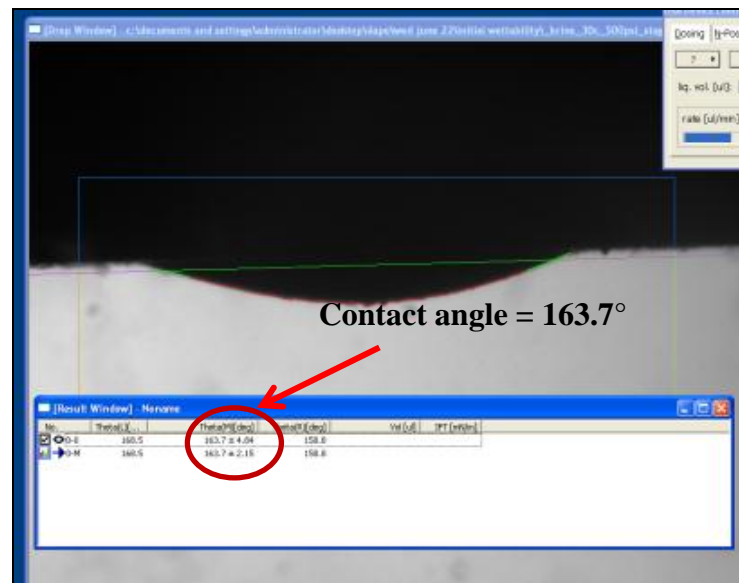


Fig.-4.1 Initial wettability was oil-wet in spent acid with HCl only

Preflush: The rock was water-wet at 54.2° after centrifuging in a spent acid solution with 10-vol% EGMBE to simulate the preflush. This shows that EGMBE dissolves the oil on the formation pore surface and makes the rocks water-wet (**Fig. 4.2**).

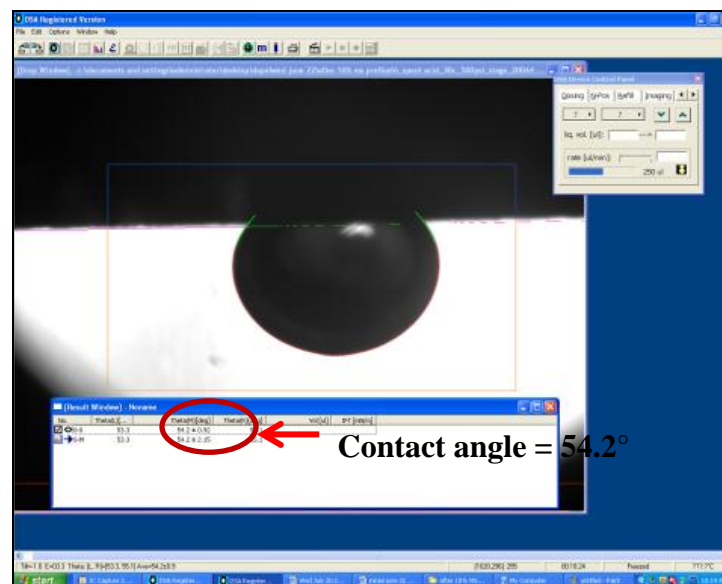


Fig.-4.2 Wettability changed to water-wet after a 10-vol% EGMBE preflush

Main acid stage: The rock remained water-wet after the main stage in which the rock was centrifuged in a spent acid solution with HCl only. This was because there were no surface-active agents in the spent acid.

Diverting stage: Centrifuging in a spent acid solution with 4-vol% VES “A” simulated the diversion stage. This resulted in the oil droplet initially spreading on the surface of the rock. When another droplet was injected after 20 hours, the rock was water-wet (**Fig. 4.3**).

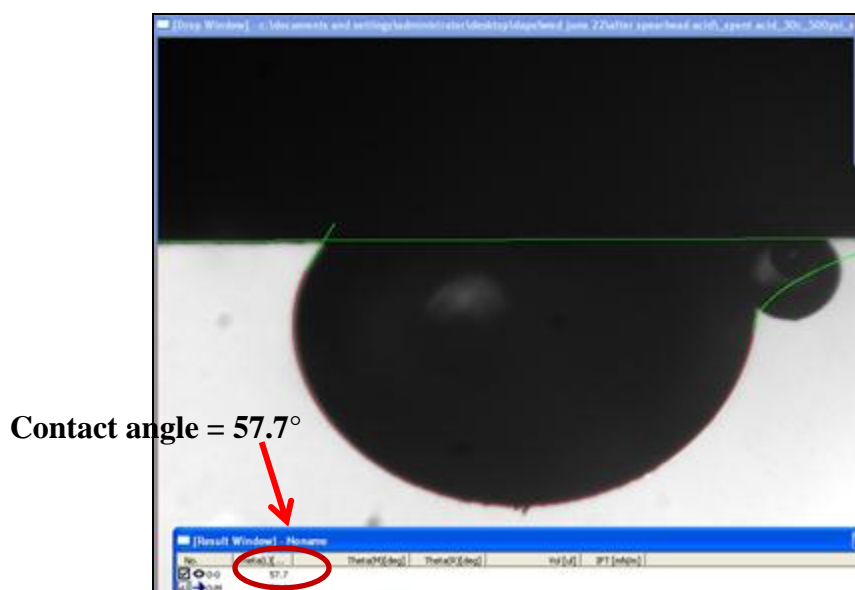


Fig.-4.3 Wettability was water-wet after a 4 vol% VES “A” diversion stage

The change in wettability suggests that there was a change in the arrangement of the surfactant molecules on the rock surface. Initially, the VES molecules were probably arranged such that the hydrophobic tail was turned towards the aqueous solution or lay parallel to the rock surface (**Fig. 4.4**). Therefore, the rock was oil-wet. After 20 hours,

the hydrophilic head was turned up towards the aqueous solution, thus changing the wettability to water-wet.

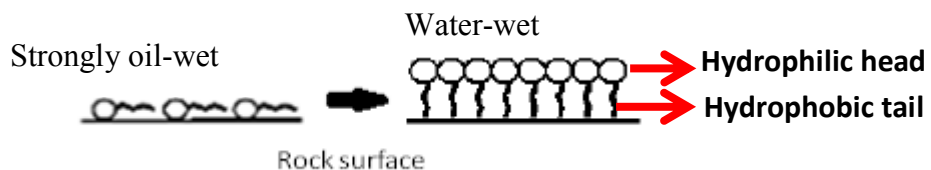


Fig.-4.4 Possible explanation for change in wettability from oil-wet to water-wet: rearrangement of VES molecules

It was also possible that the surfactant adsorbed with its hydrophobic tail, so that further adsorption resulted in the form of bilayer interaction between the hydrophilic head groups shown in **Fig. 4.5**, making the rock strongly oil-wet initially. Then surfactant desorption resulted in the loss of the upper layer of surfactant, thus changing the wettability to water-wet.

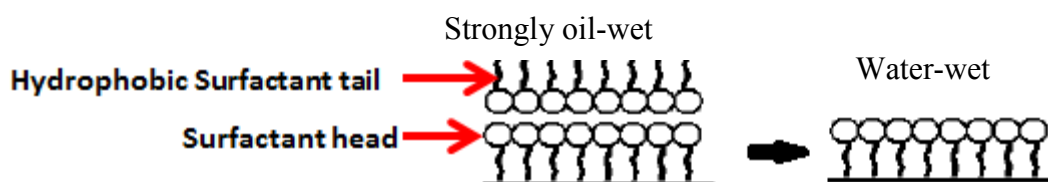


Fig.-4.5 Possible explanation for change in wettability from oil-wet to water-wet: VES desorption

This change in wettability is probably specific to the experimental conditions such as temperature, and the rock being immersed in a spent acid solution with HCl only.

Postflush: Finally, centrifuging the rock in a spent acid solution with 10-vol% EGMBE to simulate the EGMBE postflush made the rock water-wet at 50.4° (**Fig. 4.6**).

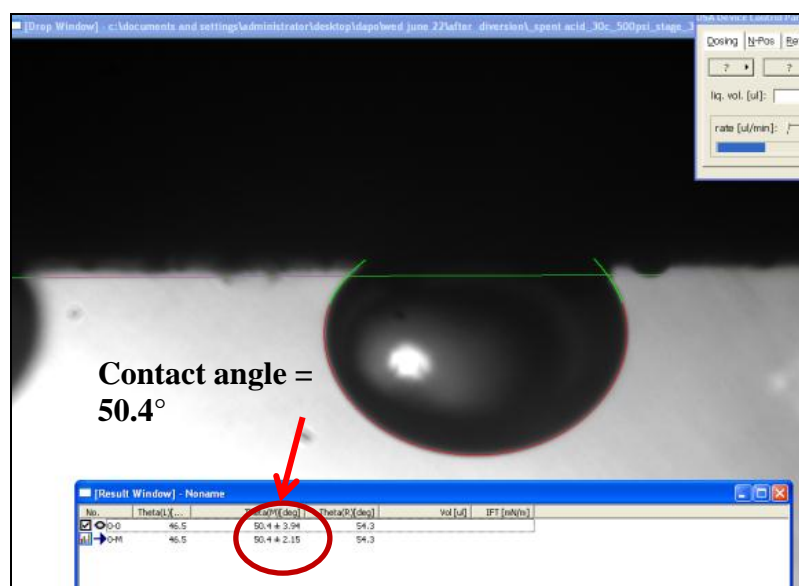


Fig.-4.6 A 10-vol% EGMBE postflush made rocks water-wet

4.2.1.2 Diversion with VES “A” and an EGMBE preflush and postflush at 80°C

Diversion with 4 vol% VES “A” with a EGMBE preflush and postflush changed wettability from oil-wet to water-wet at 80°C.

Initial wettability: The rock was initially oil-wet with a contact angle of 161-165°.

Preflush: The rock was water-wet after the 10-vol% EGMBE preflush. This shows that EGMBE dissolves the oil on the formation pore surface and makes the rocks water-wet at 25 and 80°C.

Main acid stage: The rock remained water-wet after the main stage in which the rock was centrifuged in a spent acid solution with HCl only. This was because there were no surface-active agents in the spent acid.

Diverter stage: The rock became oil-wet after centrifuging in a spent acid solution with 4-vol % VES “A”. Another droplet injected two hours later showed the

droplet to be water-wet (**Fig. 4.7**). This again suggests a change in the arrangement of the VES molecules as described in (Figs. 4.4 and 4.5).

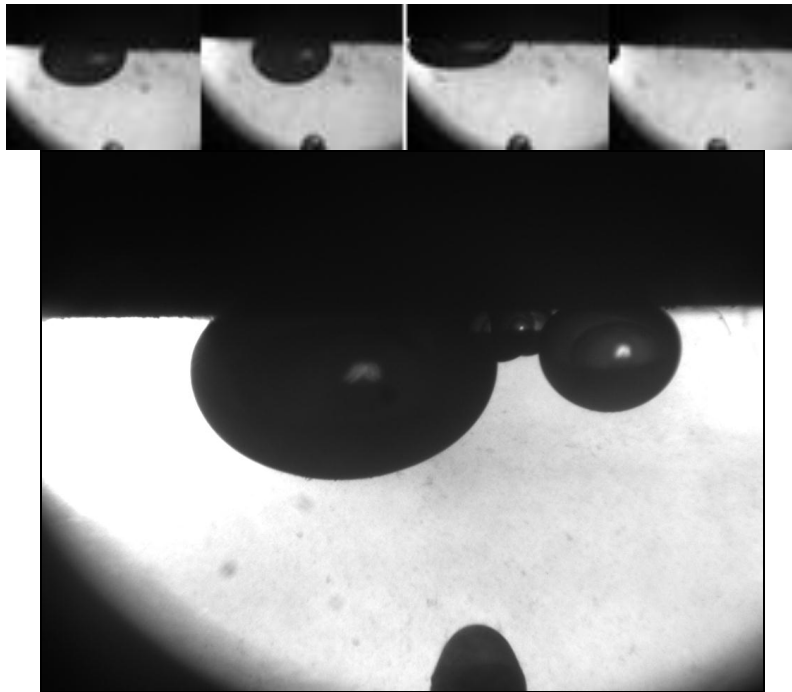


Fig.-4.7 After VES diversion with 4- vol % VES "A", the rock was initially strongly oil-wet (top), but became water-wet (bottom)

Postflush: The rock became water-wet with a contact angle of 77° after the postflush with 10-vol% EGMBE (**Fig. 4.8**).

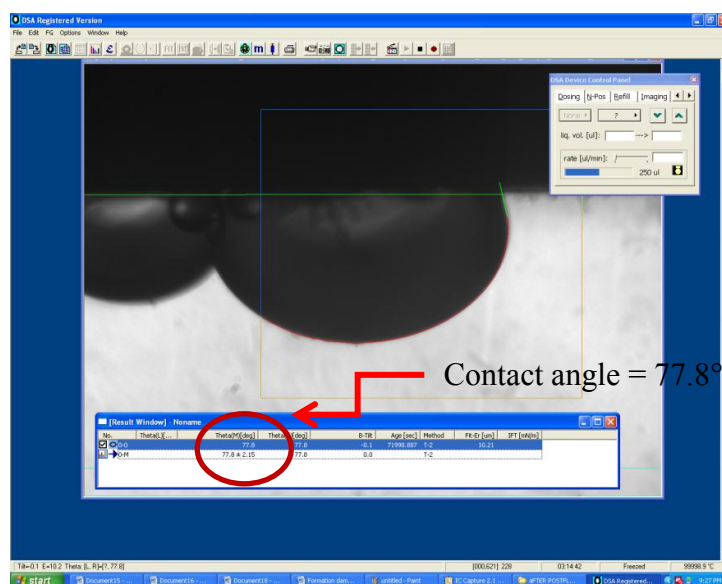


Fig.-4.8 Final wettability at 80°C after a 10-vol% EGMBE postflush was water-wet

4.2.1.3 VES “B” and EGMBE at 25 and 110°C

Similar results for VES “A” at 25 and 80°C were observed for VES “B”. A 10-vol % EGMBE preflush and postflush made oil-wet rocks water-wet following diversion with a 4-vol % VES “B” at 25 and 110°C.

4.2.1.4 Section 4.2.1 summary

Effect of an EGMBE preflush and postflush: At temperatures from 25 to 110°C, simulated acid treatments with a 10-vol % EGMBE preflush and postflush changed the wettability of rocks from oil-wet to water-wet with 4-vol% of both VES formulations as diverting stages. Results are summarized in **Fig. 4.9**.

Effect of an EGMBE preflush: A 10-vol % EGMBE preflush made oil-wet rocks water-wet after diversion stages for VES “A” at 25 and 80°C (**Fig. 4.10**). The rocks were oil-wet immediately after the diversion stage, but changed to water-wet after

about 12-20 hours. This change can be attributed to a rearrangement of VES molecules on the rock surface (Figs. 4.4 and 4.5).

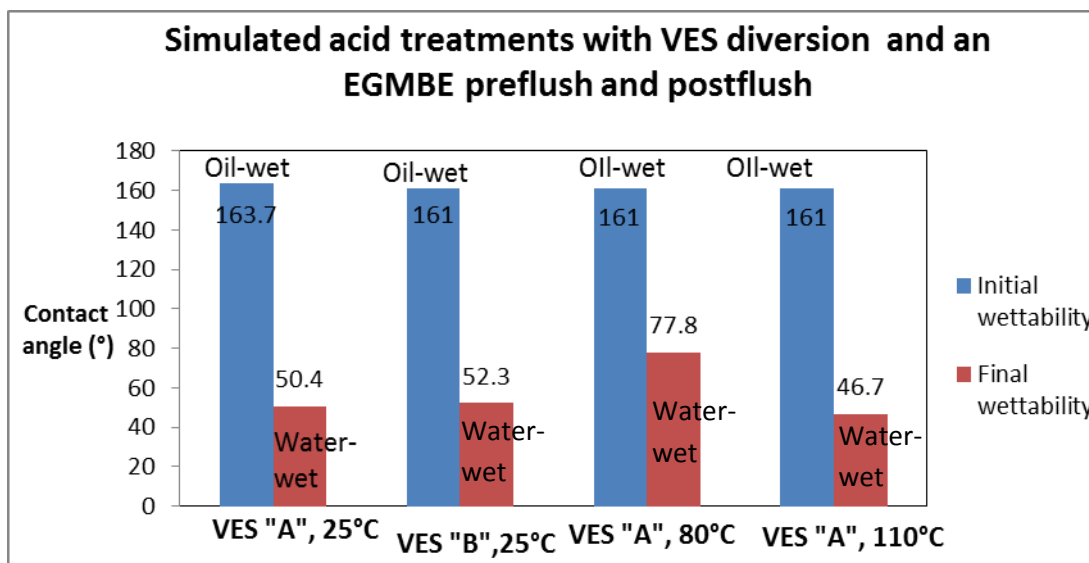


Fig.-4.9 Simulated acid treatments with an EGMBE preflush and postflush make rocks water-wet after VES diversion

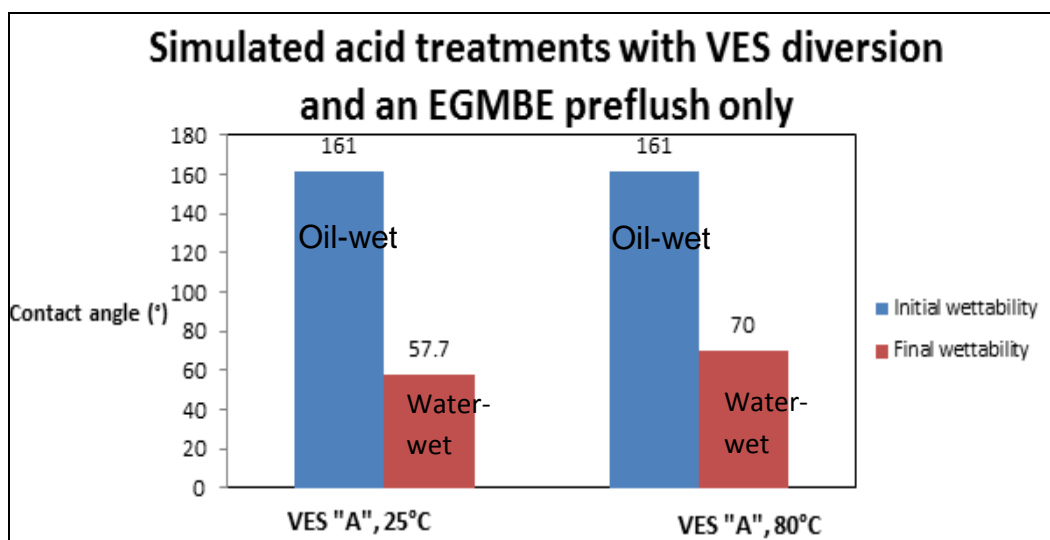


Fig.-4.10 A 10-vol % EGMBE preflush on made oil-wet rocks water-wet after diversion with 4-vol % VES "A"

4.2.2 Simulated acid treatments with a VES diversion stage only

A simulated acid treatment with a VES "A" diversion stage only changed wettability from oil-wet to water-wet at 25°C (Section 4.2.2.1).

Simulated acid treatments with a VES "A" diversion stage at 80°C and for VES "B" at 25 and 110°C were apparently strongly oil-wetting with the oil droplet spreading on the surface of the rock (Section 4.2.2.2). However, more analysis is required to determine whether spreading was due to the effect of VES and EGMBE on the rock-fluid interface, rather than on the fluid-fluid interface.

The results are summarized in Table 4.4.

Table 4.4 Effect of diversion with VES only				
VES type	VES (vol %)	Temperature °C	Initial Wettability	Diverting stage
"A"	4	25	161-165°	Oil-wet, then water-wet after 12-20 hours (71°) (56-71°)
"A"	4	80	161-165°	Strongly Oil-wet?
"B"	4	25	161-165°	Strongly Oil-wet?
"B"	6	110	161-165°	Strongly Oil-wet?

4.2.2.1 Diversion with VES "A" only at 25°C

A simulated acid treatment with diversion with 4-vol % VES "A" only made oil-wet rocks water-wet at 25°C.

Initial wettability: The rock was initially oil-wet at 25°C in spent acid with HCl only (**Fig. 4.11**) with a contact angle of 161°.

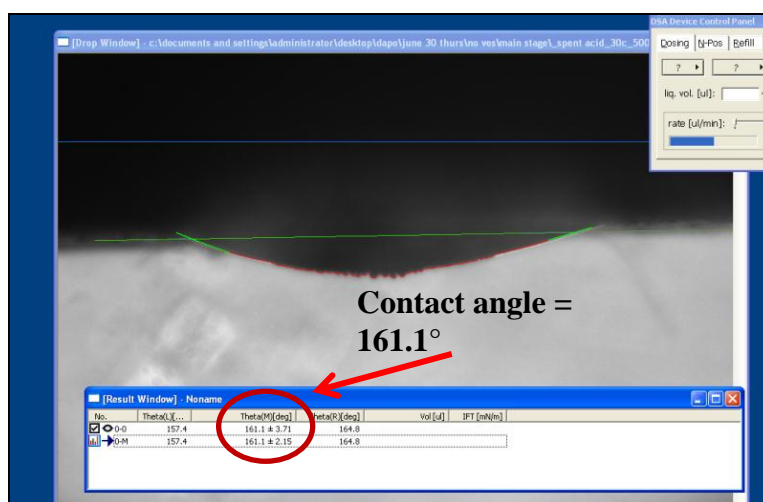


Fig.-4.11 The initial wettability in spent acid was water-wet

Main treating fluid: The rock was centrifuged in a spent acid solution with HCl only to simulate the main acid stage. The rock remained oil-wet after centrifuging. This was because there were no surfactants in spent acid with HCl only.

Diverter stage: The rock was then centrifuged in a spent acid solution with 4-vol% VES “A” only to simulate the diverter stage. It was strongly oil-wet initially after the diversion stage, with the oil-droplet spreading on the surface of the rock (**Fig. 4.12**).

After 12 hours in the spent acid solution with HCl only, another oil-droplet injected onto the rock showed it to be water-wet with a contact angle of 70.1°.

This indicates that there was a change in the arrangement of the surfactant molecules as described in Figs. 4.4 and 4.5.



VES "A" resulted in an oil-wet rock initially with the droplet spreading on the rock at 25°C

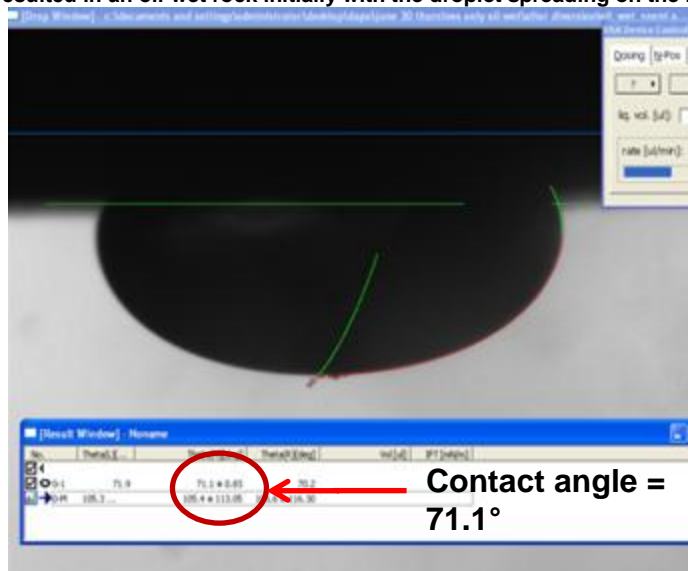


Fig.-4.12 A simulated acidizing treatment with 4 vol% VES "A" resulted in an oil-wet rock initially (top) with the droplet spreading on the rock. After 12 hours, the rock became water-wet

4.2.2.2 Diversion with VES "A" only at 80°C, and VES "B" only at 25°C and 110°C

Simulated acid treatments with a 4-vol % VES "A" diversion stage at 80°C, and 4-vol % VES "B" diversion stage at 25 and 110°C resulted in oil droplets spreading on the surface of the rock.

4 vol% VES "A" only, 80°C

Initial wettability: The rocks were initially oil-wet with a contact angle of 161-165° in spent acid with HCl only.

Main acid stage: The initially oil-wet rock was centrifuged in a spent acid solution with HCl only to simulate the main acid stage. The contact angle changed from oil-wet to initially water-wet (**Fig. 4.13**). We did not study the effect of time on

wettability. This change in wettability is in contrast with the results at 25°C (4.2.2.1). It may have occurred because an increase in temperature to 80°C made the rocks more water-wet after spent acid displaced some of the crude-oil related surfactants that were weakly adhered to the rock.



Fig.-4.13 Wettability after main acid stage was water-wet initially

Diverting stage: To simulate the diversion stage, the rock was centrifuged in a spent acid solution with 4-vol% VES “A”. The oil droplet spread on the surface of the rock at 80°C initially. When another droplet was injected after 24 hours, the oil droplet also spread (**Fig. 4.14**). This was in contrast with the result at 25°C, which was water-wet after 12 hours (Section 4.2.2.1).

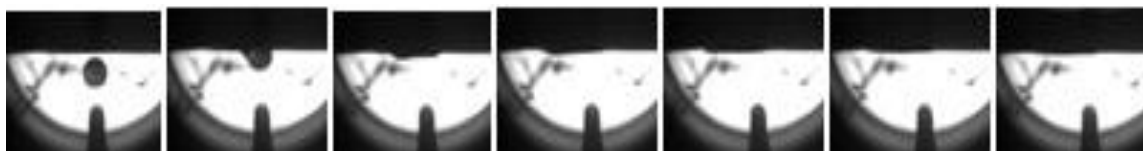


Fig.-4.14 Wettability after diversion stage

Similar results were obtained for 4-vol % VES “B” at 25 and 110°C.

4.2.2.3 Section 4.2.2 Summary: Effect of VES diversion only

Our simulated acid treatments with a VES diversion stage with no EGMBE preflush and postflush show that:

1. Diversion with 4-vol % VES “A” only at 25°C resulted in initially strongly oil-wet rocks, which changed to water-wet with time (**Fig. 4.15**).
2. Oil droplets spread on the rock for simulated acid treatments with VES “B” only at 25°C and 110°C, and VES “A” at 80°C (Fig. 4.15).

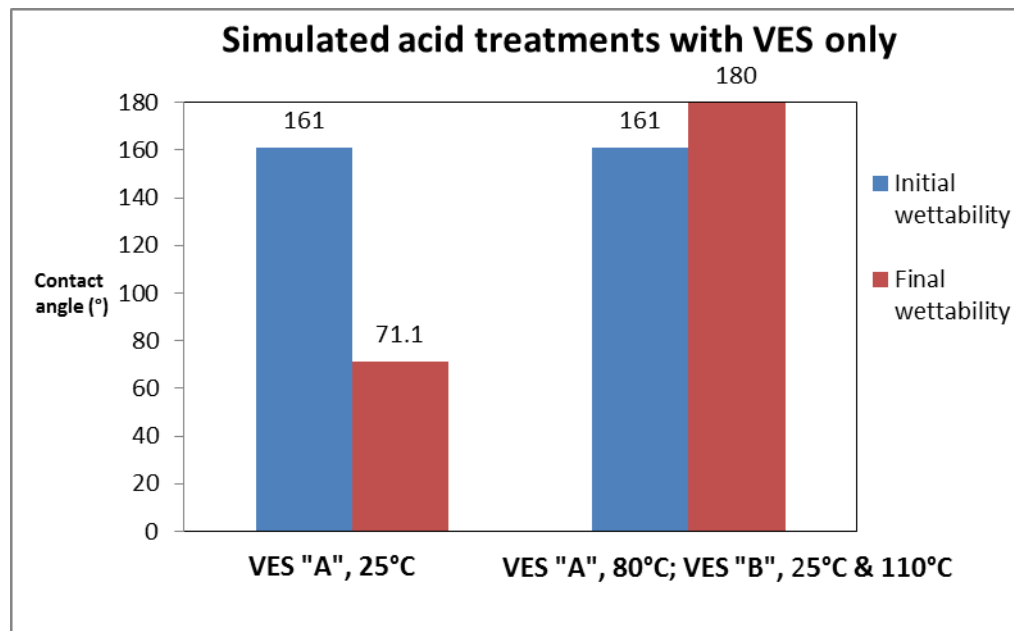


Fig.-4.15 Effect of simulated acid treatments with VES diversion only on wettability

The possible explanation for the spreading oil droplets in Fig. 4.15 are:

- a. The rearrangement of VES on the surface or the rock as happened for the spent acid with VES “A” at 25°C (Figs. 4.4 and 4.5) was not energetically favorable. Therefore, the rocks remained strongly oil-wet.

- b. VES adsorbed electrostatically (**Fig. 4.16**) so that the rock was strongly oil-wet.

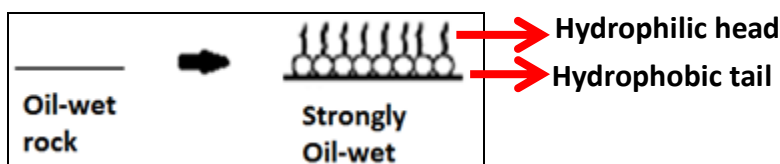


Fig.-4.16 Possible explanation for spreading of oil droplets in Fig. 4.15 – Electrostatic adsorption

- c. Surfactant desorption from the rock surface reduced the oil-acid IFT below the critical spreading tension.

There was evidence of surfactant desorption from the rock surface in some of our results as indicated by wettability changes during contact angle measurements (Fig. 4.5).

Equipment limitations did not allow us to measure the oil-acid IFT at the same time as contact angle experiments were being performed. However, an accurate interpretation of the results for spreading oil droplets requires that we know the oil-acid IFT below which oil droplets spread (the critical spreading tension, Section 3.4.1).

The critical spreading tension will be less than or equal to the IFT between oil and spent acid for which oil droplets did not spread during contact angle experiments (e.g. in Fig. 4.12). If the oil-acid IFT for the spreading oil droplets in Fig. 4.14 is greater than the oil-acid IFT in Fig. 4.12, then the spreading can be attributed to surfactant adsorption at the rock-fluid interface. If the IFT is less, then the spreading may be a reflection of the effect of VES and EGMBE on the fluid-fluid interface.

4.3 Section 4 conclusions

Simulated acid treatments with the new procedure for receding contact angle experiments showed that:

1. A 10-vol% EGMBE preflush and postflush after diversion with 4-vol% VES “A” and “B” at 25, 80, and 110°C make oil-wet rocks water-wet (Fig. 4.9)
2. A 10-vol % EGMBE preflush made oil-wet rocks water-wet after the diversion stage for 4-vol% VES “A” at 25 and 80°C (Fig. 4.10).
3. A 4-vol % VES “A” diversion stage without an EGMBE postflush or postflush was strongly oil-wet initially, and then water-wet at 25°C (Fig. 4.15). This wettability change is probably specific to the experimental conditions.
4. A 4-vol % VES “A” diversion stage at 80°C, and a 4-6 vol% VES “B” diversion stage at 25 and 110°C without an EGMBE postflush or postflush caused oil droplets to spread. An accurate interpretation of these results requires that spreading is known to be due to changes at the rock-fluid interface rather than the fluid-fluid interface.

These results represent the wettability just as starts to displace spent acid.

The procedure for contact angle experiments will help engineer’s design better acid treatments by allowing them investigate the effect of different treating fluid-diverter sequences on wettability.

5 CONCLUSIONS

Carbonate reservoirs are heterogeneous; therefore, proper acid placement/diversion is required to make matrix acid treatments effective. Viscoelastic surfactants (VES) are used as diverting agents in carbonate matrix acidizing. However, these surfactants can adversely affect wettability around the wellbore area. Water-wetness is the desired wettability state to maximize oil production after an acid treatment.

We studied the effect of two amphoteric amine-oxide viscoelastic surfactants and the mutual solvent (EGMBE) on the wettability of Austin Cream Chalk samples using static receding contact angle experiments.

Lungwitz et al (2007) found that spent acid solutions with VES and EGMBE were water-wetting. We extended their study by measuring surfactant adsorption, studying the effect of temperature on wettability, using rocks that were prepared to simulate reservoir conditions, and providing a detailed procedure for contact angle experiments. Temperatures were varied from 25 to 110°C, VES concentrations from 1-6 vol% and the EGMBE concentration was 10-vol%.

Two-phase titration experiments show that:

1. VES “A” and “B” adsorb on Austin Cream Chalk at 25, and 80°C. Wettability changes observed in the contact angle experiments can be attributed to VES adsorption.

Our literature review showed that surfactant wettability studies measure advancing contact angles, representing wettability in EOR. Receding contact angle experiments are representative of wettability for stimulation treatments. We used conventional static receding contact angle experiments to study the effect of spent acid with VES and EGMBE on wettability. We found that:

2. Spent acid solutions with 1-vol % VES and 10-vol% EGMBE reduce the IFT between oil and spent acid and cause oil droplets to spread. Spreading was due to the effect of VES and EGMBE on the fluid-fluid interface, not the rock-fluid interface and so does not reflect the rock wettability.

We developed a new procedure for static receding contact angles that shows the effect of stimulation fluids on the rock-fluid interface, rather than the fluid-fluid interface. We applied the new procedure to study the effect of spent acid with VES and EGMBE, representative of mixing after an acid treatment on wettability. We found that:

3. Spent acid solutions with 1 vol % VES “A” and 10 vol% EGMBE were water-wetting (Fig. 3.14). This result is consistent with the results of Lungwitz et al (2007).

4. Spent acid solutions with 1-vol % VES “A” only were strongly oil-wetting (Fig. 3.12). This result was not consistent with Lungwitz et al (2007). However, longer observation (Section 4) shows that VES “A” has a water-wetting effect.
5. Spent acid solutions with HCl only do not change wettability (Fig. 3.17). This was because there were no surface-active agents in the surfactant.

Acid treatments consist of different treating fluid diverter sequences; therefore, we simulated acid treatments to with a preflush, main stage, diverter stage, and postflush using the new procedure. These results represent the wettability state at the rock-fluid interface just as oil starts to displace spent acid. We found from simulated acid treatments that:

6. A 10 vol% EGMBE preflush and postflush with a 4 vol% VES diversion stage made oil-wet rocks water-wet at 25, 80, and 110°C (Fig. 4.9).
7. A 10-vol% EGMBE preflush made oil-wet rocks water-wet following a diversion stage with VES 4 vol% “A” at 25 and 80°C (Fig. 4.10).
8. A 4-vol % VES “A” diversion stage without an EGMBE postflush or postflush was strongly oil-wet initially, and then water-wet at 25°C (Fig. 4.15). This change in wettability observed is probably specific to the experimental

conditions such as temperature, and the rock being immersed in a spent acid solution with HCl only.

9. A 4-vol % VES “A” diversion stage at 80°C, and a 4-6 vol% VES “B” diversion stage at 25 and 110°C without an EGMBE postflush or postflush caused oil droplets to spread. An accurate interpretation of these results requires that spreading is known to be due to changes at the rock-fluid interface rather than the fluid-fluid interface.

Our results suggest a favorable wettability for the production of oil for the conditions and parameters investigated.

The new procedure also allows the study of the effect of different treating fluid-diverter sequences on wettability. It can be applied to dynamic contact angle measurements like the DDDC technique (Rao and Girard, 1996).

5.1 Future work

1. Extend the study of the simulated acidizing experiments to:
 - a. Initially water-wet rocks;
 - b. Study the effect of acid additives, such as corrosion inhibitors, on wettability - by centrifuging porous rocks in acidizing fluids and measuring contact angles in a neutral fluid such as spent acid or formation brine, the new procedure allows the study of chemicals that darken the aqueous solution, such as corrosion inhibitors, on wettability.

2. Correlate results with other wettability measurements (e.g. Amott/USBM indices, relative permeability).

REFERENCES

- Al-Anzi, E., Al-Mutawa, M., Al-Habib, N., Al-Mumen, A., Nasr-El-Ein, H., Alvarado, O. et al. 2004. Positive Reactions in Carbonate Reservoir Stimulation. *Schlumberger Oil Field Review*.
http://www.slb.com/~media/Files/resources/oilfield_review/ors03/win03/p28_45.ashx Downloaded 1 January 2011.
- Al-Hashim, H.S., Celik, M.S., Oskay, M.M., and Al-Yousef, H.Y. 1988. Adsorption and Precipitation Behaviour of Petroleum Sulfonates from Saudi Arabian Limestone. *Journal of Petroleum Science and Engineering* **1** (4): 335-344. DOI: 10.1016/0920-4105(88)90008-3
- Al-Mutawa, M., Al-Anzi, E.H.D., Jemmali, M., Chang, F.F., Samuel, E., and Samuel, M.M. 2005. Zero Damaging Stimulation and Diversion Fluid: Field Cases from the Carbonate Formations in North Kuwait. *SPE Production & Operations* **20** (2). DOI: 10.2118/80225-pa
- Anderson, W. 1986. Wettability Literature Survey- Part 2: Wettability Measurement. *SPE Journal of Petroleum Technology* **38** (11): 1246-1262. DOI: 10.2118/13933-pa
- Anderson, W.G. 1987. Wettability Literature Survey Part 5: The Effects of Wettability on Relative Permeability. *SPE Journal of Petroleum Technology* **39** (11): 1453-1468. DOI: 10.2118/16323-pa
- Ayirala, S.C. and Rao, D.N. 2004. Multiphase Flow and Wettability Effects of Surfactants in Porous Media. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **241** (1-3): 313-322.
- Ayirala, S.C., Vijapurapu, C.S., and Rao, D.N. 2006. Beneficial Effects of Wettability Altering Surfactants in Oil-wet Fractured Reservoirs. *Journal of Petroleum Science and Engineering* **52** (1-4): 261-274. DOI: 10.1016/j.petrol.2006.03.019
- Bartell, F.E., Thomas, T.L., and Fu, Y. 1951. Thermodynamics of Adsorption from Solutions. IV. Temperature Dependence of Adsorption. *The Journal of Physical Chemistry* **55** (9): 1456-1462. DOI: 10.1021/j150492a005
- Caweizel. 2007. Method of Acidizing a Subterranean Formation with Diverting Foam or Fluid. *US Patent 7303018*.

- Cayias, J.L., Schechter, R.S., and Wade, W.H. 1975. The Measurement of Low Interfacial Tension Via the Spinning Drop Technique. In *Adsorption at Interfaces*, P. 234-247, ACS Symposium Series, Washington, D. C: American Chemical Society.
- Chang, F., Qu, Q., and Frenier, W. 2001. A Novel Self-diverting-acid Developed for Matrix Stimulation of Carbonate Reservoirs. Paper presented at the SPE International Symposium on Oilfield Chemistry, Houston, Texas. 65033.
- Chang, F.F., Love, T.G., Affeld, C.J., Blevins, J.B., Thomas, R.L., and Fu, D.K. 2000. New Material and Technique for Matrix Stimulation in High-water-cut Oil Wells. *SPE Drilling & Completion* **15** (2). DOI: 10.2118/64006-pa
- Chang, F.F., Qiu, X., and Nasr-El-Din, H.A. 2007. Chemical Diversion Techniques Used for Carbonate Matrix Acidizing: An Overview and Case Histories. Paper presented at the International Symposium on Oilfield Chemistry, Houston, Texas, U.S.A. DOI: 10.2118/106444-ms.
- Chatriwala, S., Cawiezel, K.E., Nasr-El-Din, H.A., Al-Rufaie, Y.A., and Al-Tameimi, Y. 2005. A Case Study of a Successful Matrix Acid Stimulation Treatment in Horizontal Wells Using a New Diversion Surfactant in Saudi Arabia. Paper presented at the SPE Middle East Oil and Gas Show and Conference, Kingdom of Bahrain 93536-MS.
- Chilingar, G.V. and Yen, T.F. 1983. Some Notes on Wettability and Relative Permeabilities of Carbonate Reservoir Rocks, II *Energy Sources (N.Y.); (United States)* **7** (1): 67-76.
- Crews, J.B. and Huang, T. 2007. Internal Breakers for Viscoelastic Surfactant Fracturing Fluids. Paper presented at the International Symposium on Oilfield Chemistry, Houston, Texas, U.S.A. SPE 106216 - MS.
- Cuiec, L. 1989. Effect of Drilling Fluids on Rock Surface Properties. *SPE Formation Evaluation* **4** (1). DOI: 10.2118/15707-pa
- Economides, M.J. and Nolte, K.G. 2000. *Reservoir Stimulation*. Chichester Wiley.
- Esfahani, M.R. and Haghighi, M. 2004. Wettability Evaluation of Iranian Carbonate Formations. *Journal of Petroleum Science and Engineering* **42** (2-4): 257-265. DOI: 10.1016/j.petrol.2003.12.016
- Gardner, J.E. and Hayes, M.E. Undated. Instruction Manual for the University of Texas Spinning Drop Tensiometer, Model 500. In: Department of Chemistry. The University of Texas at Austin.

- Ghannam, M.T. 2003. Spreading Behavior of Crude Oil over Limestone Substrate. *Journal of Colloid and Interface Science* **262** (2): 435-441.
- Graue, A., Viksund, B.G., Eilertsen, T., and Moe, R. 1999. Systematic Wettability Alteration by Aging Sandstone and Carbonate Rock in Crude Oil. *Journal of Petroleum Science and Engineering* **24** (2-4): 85-97. DOI: 10.1016/S0920-4105(99)00033-9
- Hall, B.E. 1975. The Effect of Mutual Solvents on Adsorption in Sandstone Acidizing. *SPE Journal of Petroleum Technology* **27** (12): 1439-1442. DOI: 10.2118/5377-pa
- Harkins, W.D. and Feldman, A. 1922. Films. The Spreading of Liquids and the Spreading Coefficient. *Journal of the American Chemical Society* **44** (12): 2665-2685. DOI: 10.1021/ja01433a001
- Hinkel, J.J., Brown, J.E., Gadiyar, B.R., and Beyer, E. 2003. New Environmentally Friendly Surfactant Enhances Well Cleanup. Paper presented at the SPE European Formation Damage Conference, The Hague, The Netherlands. SPE 82214-MS.
- Hirasaki, G. and Zhang, D.L. 2004. Surface Chemistry of Oil Recovery from Fractured, Oil-wet, Carbonate Formations. *SPE Journal* **9** (6): 151-162. DOI: 10.2118/88365-pa
- Hjelmeland, O.S. and Larrondo, L.E. 1986. Experimental Investigation of the Effects of Temperature, Pressure, and Crude Oil Composition on Interfacial Properties. *SPE Reservoir Engineering* **1** (7): 321-328. DOI: 10.2118/12124-pa
- Huang, T. and Crews, J.B. 2008. Do Viscoelastic-Surfactant Diverting Fluids for Acid Treatments Need Internal Breakers? Paper presented at the SPE International Symposium and Exhibition on Formation Damage Control, Lafayette, Louisiana, USA. SPE 112484-MS.
- Jennings, J. and Alfred, R. 1975. The Effect of Surfactant-bearing Fluids on Permeability Behavior in Oil-Producing Formations. Paper presented at the Fall Meeting of the Society of Petroleum Engineers of AIME, Dallas, Texas. SPE 5635-MS.
- Jones, A.T. and Davies, D.R. 1998. Quantifying Acid Placement: The Key to Understanding Damage Removal in Horizontal Wells. *SPE Production & Operations* (08). DOI: 10.2118/50975-pa

- Li, L., Nasr-El-Din, H.A., and Cawiezel, K.E. 2010a. Rheological Properties of a New Class of Viscoelastic Surfactant. *SPE Production & Operations* **25** (3): pp. 355-366. DOI: 10.2118/121716-pa
- Li, L., Nasr-El-Din, H.A., Crews, J.B., and Cawiezel, K.E. 2010b. Impact of Organic Acids/Chelating Agents on Rheological Properties of Amidoamine Oxide Surfactant. Paper presented at the SPE International Symposium and Exhibit on Formation Damage Control, Lafayette, Louisiana, USA. SPE 128091-MS.
- Lichaa, P.M., Alpustun, H., Abdul, J.H., Nofal, W.A., and Fuseni, A.B. 1992. Wettability Evaluation of a Carbonate Reservoir Rock. In *Advances in Core Evaluation, III Reservoir Management, European Core Analysis Symposium*, ed. Worthington, P.F. and Chardaire-Riviere, C. Paris, France: Gordon and Breach Science Publishers.
- Lowe, A.C., Phillips, M.C., and Riddiford, A.C. 1973. On the Wetting of Carbonate Surfaces by Oil and Water. *Journal of Canadian Petroleum Technology* **12** (2). DOI: 10.2118/73-02-04
- Lungwitz, B.R., Fredd, C.N., Brady, M.E., Miller, M.J., Ali, S.A., and Hughes, K.N. 2007. Diversion and Cleanup Studies of Viscoelastic Surfactant-based Self-diverting Acid. *SPE Production & Operations* **22** (1): 121-127. DOI: 10.2118/86504-pa
- Mani, V. and Mohanty, K.K. 1997. Effect of the Spreading Coefficient on Three-phase Flow in Porous Media. *Journal of Colloid and Interface Science* **187** (1): 45-56.
- Mannhardt, K. and Novosad Jerry, J. 1994. Adsorption of Foam-forming Surfactants for Hydrocarbon-miscible Flooding at High Salinities. In *Foams: Fundamentals and Applications in the Petroleum Industry*, Advances in Chemistry, Washington, DC American Chemical Society.
- Mannhardt, K., Schramm, L.L., and Novosad, J.J. 1992. Adsorption of Anionic and Amphoteric Foam-forming Surfactants on Different Rock Types. *Colloids and Surfaces* **68** (1-2): 37-53.
- Mannhardt, K., Schramm, L.L., and Novosad, J.J. 1993. Effect of Rock Type and Brine Composition on Adsorption of Two Foam-forming Surfactants. *SPE Advanced Technology Series* **1** (04): 212-218. DOI: 10.2118/20463-pa
- Mohan, K., Gupta, R., and Mohanty, K.K. 2011. Wettability Altering Secondary Oil Recovery in Carbonate Rocks. *Energy & Fuels* **25** (9): 3966-3973. DOI: 10.1021/ef200449y

- Morrow, N.R. 1991. *Interfacial Phenomena in Petroleum Recovery*. New York: Marcel Dekker.
- Morrow, N.R., Lim, H.T., and Ward, J.S. 1986. Effect of Crude-oil-induced Wettability Changes on Oil Recovery. *SPE Formation Evaluation* **1** (02): 89-103. DOI: 10.2118/13215-pa
- Nasr-El-Din, H.A. 2005. Formation Damage Induced by Chemical Treatments: Case Histories. *Journal of Energy Resources Technology* **127** (3): 214-224.
- Nasr-El-Din, H.A., Al-Anazi, H.A., and Mohamed, S.K. 2000. Stimulation of Water-disposal Wells Using Acid-in-diesel Emulsions: Case Histories. *SPE Production & Operations* **15** (08): 176-182. DOI: 10.2118/65069-pa
- Nasr-El-Din, H.A., Al-Arnaout, I.H., Chesson, J.B., and Cawiezel, K.E. 2005. Novel Techniques for Improved CT Access and Stimulation in an Extended-reach Well. Paper presented at the SPE/ICoTA Coiled Tubing Conference and Exhibition, The Woodlands, Texas. 94044.
- Nasr-El-Din, H.A., Al-Ghamdi, A.H., Al-Qahtani, A.A., and Samuel, M.M. 2008. Impact of Acid Additives on the Rheological Properties of a Viscoelastic Surfactant and Their Influence on Field Application. *SPE Journal* **13** (1): 35-47. 89418. DOI: 10.2118/89418-pa
- Nasr-El-Din, H.A., Al-Habib, N.S., Al-Mumen, A.A., Jemmali, M., and Samuel, M. 2006. A New Effective Stimulation Treatment for Long Horizontal Wells Drilled in Carbonate Reservoirs. *SPE Production & Operations* **21** (3): 330-338. DOI: 10.2118/86516-pa
- Nasr-El-Din, H.A., Al-Habib, N.S., Jemmali, M., Lahmadi, A., and Samuel, M. 2004. A Novel Technique to Acidize Horizontal Wells with Extended Reach. Paper presented at the SPE Annual Technical Conference and Exhibition, Houston, Texas. 90385.
- Nasr-El-Din, H.A., Al-Mohammed, A.M., Al-Aamri, A.D., Al-Fahad, M.A., and Chang, F.F. 2009. Quantitative Analysis of Reaction-rate Retardation in Surfactant-based Acids. *SPE Production & Operations* **24** (1): 107-116. DOI: 10.2118/107451-pa
- Nasr-El-Din, H.A., Chesson, J.B., Cawiezel, K.E., and Vine, C.S.D. 2006a. Lessons Learned and Guidelines for Matrix Acidizing with Viscoelastic Surfactant Diversion in Carbonate Formations. Paper presented at the SPE Annual Technical Conference and Exhibition, San Antonio, Texas, USA. SPE 102468 - MS.

- Nasr-El-Din, H.A., Chesson, J.B., Cawiezel, K.E., and Vine, C.S.D. 2006b. Investigation and Field Evaluation of Foamed Viscoelastic Surfactant Diversion Fluid Applied During Coiled-Tubing Matrix-Acid Treatment. Paper presented at the SPE/ICoTA Coiled Tubing Conference & Exhibition, The Woodlands, Texas, USA. SPE 99651-MS.
- Nasr-El-Din, H.A., Chesson, J.B., Cawiezel, K.E., and Vine, C.S.D. 2006c. Field Success in Carbonate Acid Diversion, Utilizing Laboratory Data Generated by Parallel Flow Testing. Paper presented at the SPE Annual Technical Conference and Exhibition, San Antonio, Texas, USA. SPE 102828-MS.
- Nasr-El-Din, H.A., Erbil, M., and El-Gamal, S.K.M. 2005. Successful Application of Foamed Viscoelastic Surfactant-Based Acid. Paper presented at the SPE European Formation Damage Conference, Sheveningen, The Netherlands. SPE 95006.
- Nasr-El-Din, H.A., Samuel, E., and Samuel, M. 2003. Application of a New Class of Surfactants in Stimulation Treatments. Paper presented at the SPE International Improved Oil Recovery Conference in Asia Pacific, Kuala Lumpur, Malaysia. Society of Petroleum Engineers 84898-MS.
- Nasr-El-Din, H.A. and Samuel, M.M. 2007. Lessons Learned from Using Viscoelastic Surfactants in Well Stimulation. *SPE Production & Operations* **22** (1): 112-120. SPE 90383-PA. DOI: 10.2118/90383-pa
- Oren, P.E. and Pinczewski, W.V. 1994. The Effect of Wettability and Spreading Coefficients on the Recovery of Waterflood Residual Oil by Miscible Gasflooding. *SPE Formation Evaluation* **9** (2): 149-156. DOI: 10.2118/24881-pa
- Owens, W.W. and Archer, D.L. 1971. The Effect of Rock Wettability on Oil-Water Relative Permeability Relationships. *SPE Journal of Petroleum Technology* **23** (7): 873-878. DOI: 10.2118/3034-pa
- Penny, G.S., Conway, M.W., and Briscoe, J.E. 1983. Enhanced Load Water-Recovery Technique Improves Stimulation Results. Paper presented at the SPE Annual Technical Conference and Exhibition, San Francisco, California. Society of Petroleum Engineers of AIME 12149-MS
- Rao, D. 2003. The Concept, Characterization, Concerns and Consequences of Contact Angles in Solid-liquid-liquid Systems. *Contact Angle, Wettability and Adhesion* **3**: 191-210.
- Rao, D.N. 1999. Wettability Effects in Thermal Recovery Operations. *SPE Reservoir Evaluation & Engineering* **2** (5): 420-430. DOI: 10.2118/57897-pa

- Rao, D.N. and Girard, M.G. 1996. A New Technique for Reservoir Wettability Characterization. *Journal of Canadian Petroleum Technology* **35** (01). DOI: 10.2118/96-01-05
- Río, O.I.D. and Neumann, A.W. 1997. Axisymmetric Drop Shape Analysis: Computational Methods for the Measurement of Interfacial Properties from the Shape and Dimensions of Pendant and Sessile Drops. *Journal of Colloid and Interface Science* **196** (2): 136-147.
- Rosen, M.J. and Dahanayake, M. 2000. *Industrial Utilization of Surfactants - Principles and Practice*. Urbana, Illinois: AOCS Press.
- Safwat, M., Nasr-El-Din, H.A., Dossary, K., McClelland, K., and Samuel, M. 2002. Enhancement of Stimulation Treatment of Water Injection Wells Using a New Polymer-free Diversion System. Paper presented at the Abu Dhabi International Petroleum Exhibition and Conference, Abu Dhabi, United Arab Emirates. 78588.
- Sanchez, J.M. and Hazlett, R.D. 1992. Foam Flow through an Oil-wet Porous Medium: A Laboratory Study. *SPE Reservoir Engineering* **7** (1): 91-97. DOI: 10.2118/19687-pa
- Sayyoun, M.H., Hemeida, A.M., Al-Blehed, M.S., and Desouky, S.M. 1991. Role of Polar Compounds in Crude Oils on Rock Wettability. *Journal of Petroleum Science and Engineering* **6** (3): 225-233. DOI: 10.1016/0920-4105(91)90015-f
- Scamehorn, J.F., Schechter, R.S., and Wade, W.H. 1982. Adsorption of Surfactants on Mineral Oxide Surfaces from Aqueous Solutions: I: Isomerically Pure Anionic Surfactants. *Journal of Colloid and Interface Science* **85** (2): 463-478. DOI: 10.1016/0021-9797(82)90013-3
- Schramm, L.L. and Mannhardt, K. 1996. The Effect of Wettability on Foam Sensitivity to Crude Oil in Porous Media. *Journal of Petroleum Science and Engineering* **15** (1): 101-113.
- Seethepalli, A., Adibhatla, B., and Mohanty, K.K. 2004. Physicochemical Interactions During Surfactant Flooding of Fractured Carbonate Reservoirs. *SPE Journal* **9** (4): 411-418. DOI: 10.2118/89423-pa
- Shimizu, I., Itachida, O., Kobayashi, O., Haq, S.A., Nepia, P., Ajaj, M. et al. 2005. Surfactant-Based Self-Diverting Acid System Maximises Acid Coverage and Eliminates Flowback in an Openhole Horizontal Injection Well Offshore Qatar. Paper presented at the International Petroleum Technology Conference, Doha, Qatar. 10445-MS.

- Somasundaran, P. and Hanna, H.S. 1985. Adsorption/Desorption of Sulfonate by Reservoir Rock Minerals in Solutions of Varying Sulfonate Concentrations. *SPE Journal* **25** (06): 343-350. DOI: 10.2118/10603-pa
- Standnes, D.C. and Austad, T. 2000a. Wettability Alteration in Chalk: 1. Preparation of Core Material and Oil Properties. *Journal of Petroleum Science and Engineering* **28** (3): 111-121. DOI: 10.1016/s0920-4105(00)00083-8
- Standnes, D.C. and Austad, T. 2000b. Wettability Alteration in Chalk: 2. Mechanism for Wettability Alteration from Oil-wet to Water-wet Using Surfactants. *Journal of Petroleum Science and Engineering* **28** (3): 123-143. DOI: 10.1016/s0920-4105(00)00084-x
- Standnes, D.C. and Austad, T. 2003b. Wettability Alteration in Carbonates: Interaction between Cationic Surfactant and Carboxylates as a Key Factor in Wettability Alteration from Oil-wet to Water-wet Conditions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **216** (1-3): 243-259. DOI: 10.1016/s0927-7757(02)00580-0
- Taylor, K.C., Al-Ghamdi, A.H., and Nasr-El-Din, H.A. 2004. Effect of Additives on the Acid Dissolution Rates of Calcium and Magnesium Carbonates. *SPE Production & Operations* **19** (3): 122-127. DOI: 10.2118/80256-pa
- Taylor, K.C. and Nasr-El-Din, H.A. 2002. Coreflood Evaluation of In-situ Gelled Acids. Paper presented at the International Symposium and Exhibition on Formation Damage Control, Lafayette, Louisiana. DOI: 10.2118/73707-ms.
- Tiab, D. and Donaldson, E.C. 1996. *Petrophysics: Theory and Practice of Measuring Reservoir Rock and Fluid Transport Properties*. Houston, Texas: Gulf Pub. Co.
- Treiber, L.E. and Owens, W.W. 1972. A Laboratory Evaluation of the Wettability of Fifty Oil-producing Reservoirs. *SPE Journal* **12** (6): 531-540. 3526. DOI: 10.2118/3526-pa
- Wang, W. and Gupta, A. 1995. Investigation of the Effect of Temperature and Pressure on Wettability Using Modified Pendant Drop Method. Paper presented at the SPE Annual Technical Conference and Exhibition, Dallas, Texas, 1995. DOI: 10.2118/30544-ms.
- Xu, W., Ayirala, S.C., and Rao, D.N. 2008. Measurement of Surfactant-induced Interfacial Interactions at Reservoir Conditions. *SPE Reservoir Evaluation & Engineering* **11** (1): pp. 83-94. DOI: 10.2118/96021-pa

- Yu, M., Mahmoud, M., and Nasr-El-Din, H.A. 2010. Propagation and Retention of Viscoelastic Surfactants Following Matrix Acidizing Treatments in Carbonate Cores. Paper presented at the SPE International Symposium and Exhibiton on Formation Damage Control, Lafayette, Louisiana, USA. SPE 128047.
- Yu, M. and Nasr-El-Din, H.A. 2009. Quantitative Analysis of Viscoelastic Surfactants. Paper presented at the SPE International Symposium on Oilfield Chemistry, The Woodlands. Texas. SPE 121715.
- Zhang Leslie, D., Liu, S., Puerto, M., Miller, C.A., and Hirasaki, G.J. 2006. Wettability Alteration and Spontaneous Imbibition in Oil-wet Carbonate Formations. *Journal of Petroleum Science and Engineering* **52** (1-4): 213-226. DOI: 10.1016/j.petrol.2006.03.009

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